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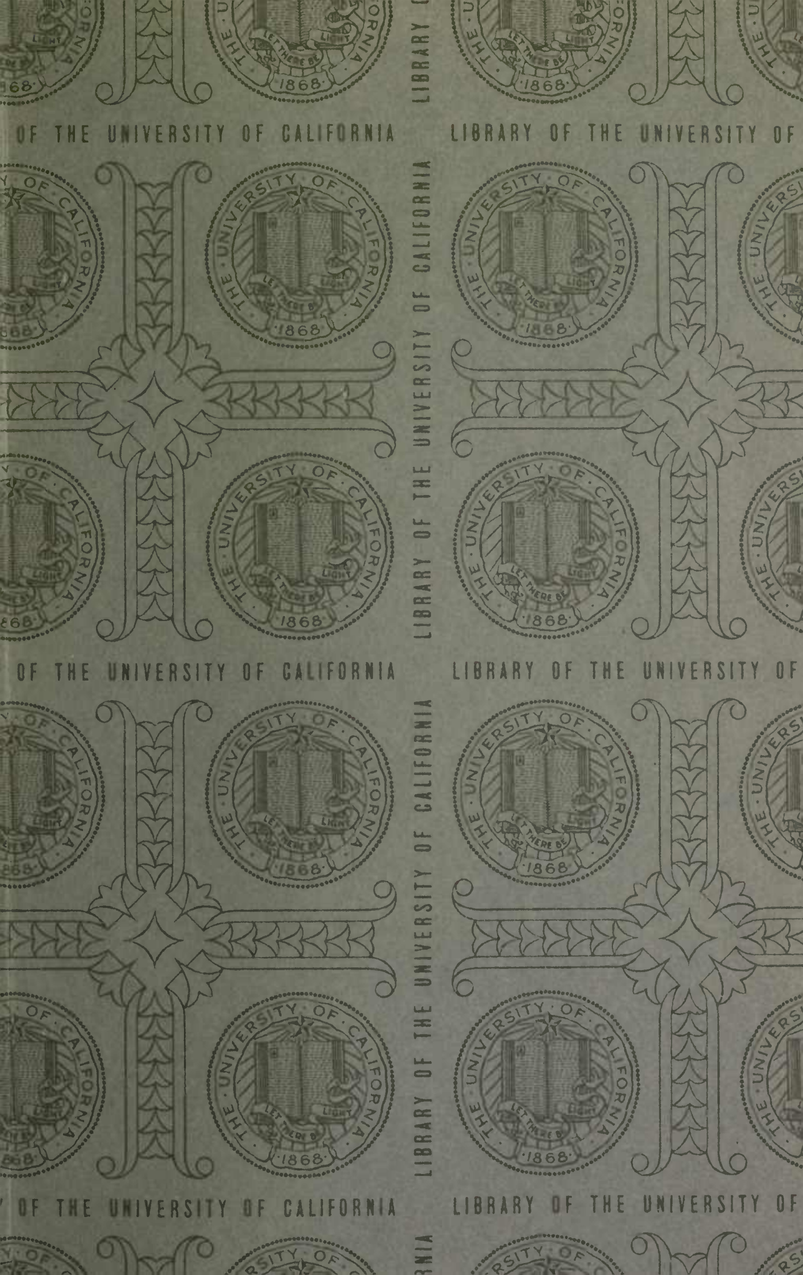

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AN EXPERIMENTAL COURSE OF PHYSICAL CHEMISTRY

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AN EXPERIMENTAL COURSE
OF
PHYSICAL CHEMISTRY

PART I
STATICAL EXPERIMENTS

BY

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PREFACE

An experience of teaching Physical Chemistry, extending over several years, has shown the author that unless the student actually performs physico-chemical experiments and verifies physico-chemical laws for himself in the laboratory, he is apt to regard the subject from too academic a standpoint. He may become interested in its principles either for their own sake, or for the purpose of passing an examination, but he does not consider it necessary that he should concern himself with its practical side. This, obviously, can only lead to a very one-sided and incomplete conception of the subject.

This work has been written, therefore, to provide the student of Physical Chemistry with a guide, which shall enable him to carry out for himself the simpler physico-chemical operations.

The lecture course on Physical Chemistry usually extends over two or more sessions, and the division of the book into two parts will thus probably prove convenient in many institutions. The first part, dealing with statical experiments, furnishes laboratory work for the first year, and therefore treats of the simpler experiments, which include those suitable for students preparing for the intermediate B.Sc. examination, and also those suitable for students in their first years' work for the Final B.Sc. examination. The second part deals with dynamical

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experiments, which are more difficult to carry out, and furnishes a second years' work suitable for students reading for the B.Sc., pass and honours, final examinations. Both parts of this work, it is hoped, will be found useful for students preparing for the examinations of the Institute of Chemistry.

The experiments chosen have been, in most cases, performed by my own students, and they do not demand any exceptional experimental skill. The two parts of the book are entirely independent of one another, although generally a knowledge of the subject-matter of Part I. has been assumed in Part II.

It is not suggested that each student should carry out every experiment. It may be left to the teacher to make a suitable selection, and in many cases the experiments under a given heading might be advantageously divided amongst the whole class, some doing one, others another. In this way each student will become acquainted with the whole.

In conclusion I wish to acknowledge my indebtedness to Ostwald-Luther's *Physiko-chemische Messungen*; to my colleague Mr. Holland Crompton, Lecturer in Chemistry at Bedford College, who, by much kindly criticism and advice, has considerably lightened the labour of writing this book, and who has read both the manuscript and proof-sheets; and also to Miss M. Walker for her assistance in correcting the proof-sheets.

J. F. SPENCER.

BEDFORD COLLEGE,
(UNIVERSITY OF LONDON),
June, 1911.

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AN EXPERIMENTAL COURSE OF PHYSICAL CHEMISTRY

CHAPTER I

INTERPRETATION OF RESULTS

PHYSICAL CHEMISTRY is a subject which deals with the investigation of chemical problems by the methods of pure physics. Its results are therefore always expressed in numbers, which for the purposes of pure chemistry must be interpreted into the language of chemistry.

In only a very limited number of cases are these numbers the outcome of a single observation, more often they are obtained by a series of more or less complicated calculations, based on one or more experimental observations.

Experimental results in physical chemistry, and indeed in any exact science, can only have their fullest value, when their probable degree of accuracy is known and taken account of in all calculations which may be based on them. The probable accuracy can only be known when due attention is paid to the exactitude of the various determinations, and when care is taken to obviate, if possible, or at least to estimate any errors which may arise in the course of the observations.

Errors may be roughly divided into two groups: **Constant Errors** and **Accidental Errors.**

Constant Errors generally arise from the presence of some factor in an experiment, which is altogether unsuspected by the observer, and which, consequently, cannot be taken into account by him. Thus, a series of careful determinations may be made of some physical property, and a value obtained, which varies but little in the several experiments; yet this value may be far removed from the true value of the selected property, because of an unsuspected constant source of error.

Constant errors can only be identified as such, when the determination is carried out by a variety of methods, differing as far as possible in their nature and in the principles underlying them, and by using materials which have been prepared by different processes or drawn from various sources.

Thus, prior to 1892, many experienced investigators had determined the density of nitrogen, and were fairly agreed upon a value, yet, despite the fact that the utmost care had been lavished on their determinations, the value obtained was false. The reason was an unsuspected constant error, namely, the presence of argon in the atmospheric nitrogen which they had used. In 1892 Rayleigh, in the course of a series of density determinations, found that atmospheric nitrogen was heavier than nitrogen obtained from other sources. This obviously pointed to a source of error in the determination of the density of nitrogen, and, on further investigation by Rayleigh and Ramsay, it was shown that all previous density determinations of nitrogen were too high, owing to the presence of argon, etc., in the material used for the measurements.

Accidental Errors arise from inaccurate observation due to accidental conditions. Thus, in determining weight, a figure may be wrongly copied down; in a titration the burette may be wrongly read, or the end point misjudged owing to failing light, and many other obvious causes. Errors of this type are accidental, and with more care, and repetition of the determination a sufficient number of times, can be entirely eliminated. When all constant errors have been removed, and when accidental errors have been guarded against, the results obtained are never quite accurate in the strictest sense of the word. They are always associated with an error which is variable, but which cannot be removed, depending upon the sensitiveness of the apparatus employed, the stability of the substances used, and the skill of the experimenter. These errors are classed together as **Experimental Errors.**

The accuracy of experiments is, therefore, limited by the exactness with which the conditions can be defined and reproduced, by the sensitiveness of the apparatus employed, by the stability of the substances examined, and by the skill of the operator.

These various causes of experimental error lead, in the course of a series of experiments, to a series of values which fluctuate about a mean value, representing the most accurate that can be obtained by the stated conditions of the experiments. The mean value is liable to be incorrect by an amount which can be calculated, and which is known as the probable error.

Recording of Observations. In recording the result of a physical determination, just so many figures should be employed as the sensitiveness of the apparatus, and the reliability of the materials, justify. Thus, if a substance be weighed on a rough balance, which is designed to weigh to 0·1 gram, it is useless to express the result to 2 or 3 decimal places, and in the same way if a volatile liquid be weighed in an open vessel, it is equally useless to record the result to more than 1 or 2 places of decimals, depending on the liquid, for the weight of such a liquid under such conditions cannot be defined more accurately than this, on account of its high vapour pressure and consequent evaporation. In entering a result into a note book, all the figures which have been determined, subject to the above mentioned restrictions, should be recorded.

Thus, suppose a weight has been determined and found to be 5·870, in such a case the last decimal figure, even though it is zero, should and must be written down. The two numbers, 5·87 and 5·870, although numerically equal, express very different results; 5·87 states that the substance weighed more than 5·87 and less than 5·88, and that it was nearer 5·87 than 5·88; on the other hand 5·870 states that the substance weighed more than 5·870, and less than 5·871. The difference between the two expressions being, if the unit of weight is the gram, that the former, 5·87, is accurate to the nearest centigram, whilst the latter, 5·870, is accurate to the nearest milligram.

Calculations from the Results of Observations. In making calculations from experimentally determined numbers, it must always be remembered that the final result cannot be more accurate than the least accurate of the experimental numbers. Thus, if several numbers have to be added together, *e.g.*

$$\begin{array}{r} 15{\cdot}8 \\ 10{\cdot}128 \\ 3{\cdot}8342 \\ \hline 29{\cdot}7622 \end{array}$$

a result is obtained which gives four decimal places. The last three places in this number are quite meaning-less, for the first number, 15·8, has an apparent error of ±0·05, and consequently the sum of the three numbers must be subject to the same error. The result in such a case should be expressed by 2·97, although in practice it is advisable to retain the next figure, particularly if the value has to be used for further calculations. The same remarks apply equally to multiplication and division. If, for example, the product of the two numbers, 1·32 and 3·5241, is required, which we may assume bear the maximum error. This, in the case of the former number will be 5 in 1320 or 0·4 per cent., and in the case of the latter 5 in 350000. On multiplying, the result must have an error of at least 0·4 per cent., hence it is obviously absurd to express it as 4·651812, for this figure is inaccurate from its origin to the extent of 0·4 per cent. The result of such multiplication is adequately expressed by 4·65. All calculations, therefore, should be made from numbers which contain just so many decimal places as the limits of accuracy allow, and only in cases where these values have to be used in further calculations should one more figure, if available, be admitted.

Rounded numbers are best treated by the shortened methods of multiplication and division, and as these now form part of elementary arithmetical training, they will not be considered here.

Use of Logarithms. Much time can often be saved in calculation if logarithms are used, and if logarithms of the right number of decimal places are used, the result will be obtained, automatically, to the same degree of accuracy as the least accurate of the numbers. Logarithms containing two decimal places more than the least accurate of the numbers should always be used. Thus, if the least accurate factor entering into a calculation is 3·758, then five-figure logarithms will give the result as accurate as that factor. The number 3·758 may contain an error amounting to 5 in 37000, about 1 in 7000, five-figure logarithms have an error inherent in them of about 1 in 30000. Consequently the result will not be affected in any way by the use of logarithms. For most physico-chemical determinations, five-figure logarithms are sufficiently accurate. Quantitative analyses may be calculated with four-figure logarithms, which have an inherent error of about 1 in 3000, but for density determinations of gases, seven-figure logarithms, which are accurate to about 1 in 1000000, ought to be employed.

An exceedingly useful instrument, based on logarithms, is found in the slide rule. This, when of a length of about 25 cms., has an accuracy of 0·2 per cent., and is therefore very convenient for many calculations which do not require more accurate treatment than the above mentioned quantity.

Influence of Errors on Results. It has already been noticed that all measurements are more or less inaccurate by an amount which can be determined. The influence of these errors on the final result still remains to be considered. If we measure a quantity x, which is directly proportional to the magnitude m we wish to obtain, *i.e.* $m \propto x$ or $m = kx$, then the relative error in the value of m is the same as the relative error in the determination of x. The absolute error is, however, k times the error of measurement of x.

If the error in the measurement of x is given by dx, then m will contain an error dm, and the absolute error will be expressed by $kdx = dm$, whilst the relative error is given by

$$\frac{dx}{x} = \frac{dm}{m}.$$

As an example of this type of measurement, we can consider the case of the determination of the pressure of a given volume of a gas from knowledge of its temperature.

It is known that $p \propto \mathsf{T}$, *i.e.* $p = k\mathsf{T}$, where p is the pressure, and T the absolute temperature of the gas. Here, if the measurement of the temperature is inaccurate by 1 per cent., the pressure calculated will also be inaccurate to the same amount.

The same relationships hold if $m \propto \frac{1}{x}$, *i.e.* $m = \frac{k}{x}$; in this case the relative error is given by the expression

$$\frac{dm}{m} = -\frac{dx}{x},$$

and the absolute error by

$$dm = -\frac{k}{x^2}dx.$$

If, in such a case as the determination of the pressure from the volume of a given quantity of a gas, the volume is measured with an error of ±2 per cent., then the pressure will be defined to the same degree of accuracy.

If the value to be determined is proportional to the square of the measured quantity, *i.e.* $m = kx^2$, the relative error will be given by

$$\frac{dm}{m} = \frac{2dx}{x},$$

and the absolute error by

$$dm = 2kxdx.$$

The relative error here is twice as great as that of the experiment, so that if the inaccuracy in the experiment amounts to 0·1 per cent., the determined value will contain an error of 0·2 per cent.

Taking now a general case where $m=kx^n$, the relative error is given by

$$\frac{dm}{m}=\frac{ndx}{x},$$

which means that the relative error of the calculated quantity is n times the experimental error.

In a series of experiments it is well to consider the relationships in which the measurements stand to the desired result, and then, remembering that the final error is practically fixed by the least accurate of the measurements, precautions can be taken to ensure that the least accurate measurement shall be determined sufficiently exactly to give a result of the desired accuracy. Further, a little consideration of this kind will often show that certain factors need not be known as exactly as it is possible to obtain them, and much time and labour will thereby be saved.

Calculation of Mean Values. It is possible to calculate, from a series of determinations of a given quantity, the most probable mean value, and also the probable error associated with that value, and with each individual determination. Thus, if $m_1, m_2, m_3, m_4, \dots$, etc., represent the values obtained in a series of n determinations of a given quantity, the mean value M will be given by taking the arithmetic mean of the various determinations.

$$\mathsf{M}=\frac{m_1+m_2+m_3+m_4+\text{etc.}}{n}.$$

It is unnecessary to add together all the numbers to get the mean, and is much easier generally to add together the quantities by which the values differ from some whole number in the immediate neighbourhood, and divide the sum of these by the number of experiments. This gives the mean divergence from the chosen whole number, and on adding this mean divergence to the whole number we get the mean value of the series of experimental results.

Thus, if m_0 represents a number lying near a series of experimental numbers m_1, m_2, m_3, m_4, etc., which differ from m_0 by amounts d_1, d_2, d_3, d_4, etc., then the mean value $\mathbf{M}$ will be given by the expression

$$\mathbf{M} = m_0 + \frac{d_1 + d_2 + d_3 + d_4 + \text{etc.}}{n}.$$

As an example, a series of temperature readings can be considered: 18°·10, 18°·18, 18°·03, 17°·99, 18°·05. It will save calculation if the number chosen as a proximate figure is the smallest of the series. Then the mean value will be given by

$$17^\circ{\cdot}99 + \frac{0{\cdot}11 + 0{\cdot}19 + 0{\cdot}04 + 0 + 0{\cdot}06}{5}$$

$$= 17^\circ{\cdot}99 + 0^\circ{\cdot}08 = 18^\circ{\cdot}07.$$

The probable error of the determinations, and of the mean value stands in close connection with the mean value.

The theory of probabilities teaches, that if e represents the probable error of each determination, and δ_1, δ_2, δ_3, δ_4, etc., the amounts by which the various determinations differ from the mean value, and n the number of determinations, then

$$e = \pm\sqrt{\frac{\delta_1^2 + \delta_2^2 + \delta_3^2 + \delta_4^2 + \text{etc.}}{(n-1)}},$$

and the error of the mean value

$$\mathbf{E} = \pm\sqrt{\frac{\delta_1^2 + \delta_2^2 + \delta_3^2 + \delta_4^2 + \text{etc.}}{n(n-1)}}.$$

The example given above may be used to illustrate the method of calculation. From this we have $\delta_1 = 3$,

$\delta_2=11$, $\delta_3=4$, $\delta_4=-8$, $\delta_5=2$. The probable error in each determination is given by

$$e=\pm\sqrt{\frac{9+121+16+64+4}{4}}=\pm\sqrt{53}=\pm 7{\cdot}2.$$

Hence e, the probable error of each determination, is $\pm 0^\circ{\cdot}072$. This error can only be diminished by making the conditions of experiment more exact; repetition of the experiment only serves to define the error more exactly, but not to diminish it.

The probable error of the mean value is given by

$$\mathrm{E}=\pm\sqrt{\frac{9+121+16+64+4}{5\times 4}}=\pm\sqrt{\frac{214}{20}}=\pm 3{\cdot}3.$$

The mean value of the above determination must now be written

$$18^\circ{\cdot}07\pm 0^\circ{\cdot}033.$$

It is obvious from the expression, that the error of the mean value may be reduced to any amount by increasing the number of experiments sufficiently. Thus the error may be reduced by one half, if the number of experiments is increased to twenty.

CHAPTER II

DETERMINATION OF WEIGHT, VOLUME AND TEMPERATURE

ALL physico-chemical operations entail the measurement of one or more of the factors, weight, volume and temperature. It is essential for the proper appreciation of the results of such determinations, that the apparatus employed, *viz.* balance, weights, measuring vessels and thermometers, should be examined, both as to their accuracy and the limits of their applicability; so that in the not unusual case of inaccuracies being discovered, the necessary corrections may be determined. The determination of the inaccuracies in the graduation of exact apparatus is termed **calibration.**

1. Determination of Weight

Of all physical properties, weight is capable of measurement to the highest degree of accuracy, but the accurate definition of the weight of a substance can only be obtained when the weights employed have been carefully calibrated. Indeed, when weighing with carefully calibrated weights and a well-adjusted balance, the error of weighing is almost always less than that arising from the variability of the substance in question, *e.g.* a small weighing bottle can be weighed to five decimal places, by using an ordinary chemical balance, but of these the last place has probably no meaning at all, and the fourth place could probably not be reproduced to within one or two units, on reweighing the bottle after use. For accurate weighing it is necessary, before all things, that the balance should rest on a firm slab or bench which is uninfluenced by the vibrations of the building. This support is best obtained, when the laboratory is on the ground floor, by using slate slabs supported by pillars standing on concrete foundations. Where the laboratory is on a higher level, the balance benches should be fixed by wall brackets to the main walls, *i.e.* those walls which are built up from the foundations of the building. Balances should always be placed in a good light, but never in such a position that direct sunlight or air currents will fall upon them. When the balance has been placed in position, it must be levelled and adjusted, so that its period of oscillation and sensitiveness are of the order required for the particular kind of work in which it is to be employed.

The period of oscillation and sensitiveness can be changed by raising or lowering a small metallic ball, "gravity bob," which is attached to the beam of the balance by a long vertical screw. Raising the "gravity bob" raises the centre of gravity of the moving parts of the balance, and so increases the stability. This increases the sensitiveness of the balance, but at the same time also the time of oscillation. The sensitiveness of the balance should therefore not be driven too far, but a medium one chosen. The best results with the modern short-beam balances are those obtained with a sensitiveness which is accompanied by a period of oscillation of 6-10 seconds.

Determination of the Sensitiveness of a Balance. Before using a balance for any purpose whatsoever, its zero point must be determined, and this process should be repeated from time to time, since the zero point is liable to change when the balance is in constant use. The zero point is the position in which the unloaded balance would come to rest if left swinging. To determine this point, the beam of the balance is released and allowed to swing freely without load. After one complete oscillation the extreme points on the scale reached by the pointer, both on the right and left of the middle point, are carefully noted during two complete oscillations. This furnishes five readings, two on the one side of the middle point and three on the other side. The arithmetic mean of each set of readings is taken, and the mean values give the average swing on each side of the middle point. Should these two values be alike, the zero point of the balance lies at the middle of the scale; if this is not the case, then the zero point lies at the position given by one half of the difference of the mean points. To avoid confusion, it is usual to designate the readings on the left of the middle point of the scale "negative," and those to the right "positive."

Suppose, in the determination of the zero point, the following readings were obtained:

	Readings to the left.	Readings to the right.
	$-5{\cdot}6$, $-5{\cdot}5$, $-5{\cdot}4$.	$+3{\cdot}8$, $+3{\cdot}6$
Mean	$-5{\cdot}5$	$+3{\cdot}7$

$$\text{Zero point} = \frac{-5{\cdot}5 + 3{\cdot}7}{2} = -0{\cdot}9.$$

This means that the zero of the balance lies 0·9 scale divisions to the left of the middle point. Should the zero point be not more than two scale divisions removed from the middle point, the balance may be used without further adjustment, but if the displacement of the zero is greater than this amount, adjustment must be made by means of the metallic screw flag below the "gravity bob," or by the screws situated at the ends of the beam. Chemists, in ordinary analytical work, are accustomed to weigh to four places of decimals by moving the rider along the balance beam until swings of equal length on either side of the zero point are obtained. This method of weighing is long and tedious, and may be substituted by the method of weighing by oscillations with great saving of time. Before weighing by oscillations it is first necessary to determine the sensitiveness of the balance for various loads. This is accomplished by placing weights, say 5 grams, on each pan, and determining the point of rest by the method already described. Then the weights on one side are increased by one milligram, and the point of rest again determined. One half the difference between the two points gives the sensitiveness for that particular load. The process is then repeated for 10, 15, 20, 25, . . . 50 gram loads, and the sensitiveness obtained in each case plotted as ordinates against the loads as abscissae to form a sensitiveness curve. Having prepared the curve, it is now possible to weigh by oscillations. The zero of the balance must be first of all determined, then the object to be weighed is counterbalanced by weights to the nearest milligram, and the point of rest determined.

Suppose, for example, the zero of the balance is $+0{\cdot}5$, and with a load counterbalanced by 15·893 grams, we have the mean oscillations $+5{\cdot}6$ and $-3{\cdot}8$.

The point of rest will be

$$\frac{+5{\cdot}6-3{\cdot}8}{2}=+0{\cdot}9.$$

The zero of the balance has therefore been displaced

$$0{\cdot}9-0{\cdot}5=0{\cdot}4 \text{ divisions.}$$

From the curve we find that the sensitiveness for a load of 15·89 grams is 1·8 divisions per milligram.

Hence, $\frac{0\cdot4}{1\cdot8}=0\cdot22$ milligram.

The weight of the substance in question is therefore 15·89322 grams.

In most physico-chemical determinations one is concerned only with relative weights, and therefore any difference in the lengths of the balance arms need not be considered. But should at any time an absolute weight be required, then any inequality of this kind must be taken into consideration. A correct weight may be obtained from a balance with unequal arms by the method of double weighings. The method is as follows:

A substance of true weight W is placed on the left-hand pan of the balance and exactly counterbalanced by w grams, it is then placed on the right-hand pan, and it is found that the weight w' is required to counterbalance it.

If it be now assumed that the lengths of the right and left arms of the balance are R and L respectively, we have, by taking moments about the point of suspension of the balance, the equations

$$LW=Rw \text{ and } RW=Lw';$$

from these expressions we obtain the ratio of the lengths of the balance arms

$$\frac{R}{L}=\sqrt{\frac{w'}{w}}.$$

The absolute weight W is then obtained by multiplying the weight required on the right-hand pan to counterbalance the object in question by the ratio of the lengths of the balance arms,

$$i.e. \quad W=\frac{R}{L}.w.$$

Calibration of Weights. Most sets of weights, no matter how costly, will be found on calibration to be inaccurate. Hence for precise work it is necessary that they should be calibrated, *i.e.* the errors determined.

The method described below for this purpose is due to Kohlrausch. A set of weights is made up of the following brass pieces: 50, 20, 10′, 10″, 5, 2, 1′, 1″ and 1‴ grams. To calibrate these, the 50 gram weight is placed on the left-hand pan, and the other weights, which make up 50 grams, are placed on the other pan. Should the two pans not balance, small weights are added to the lighter side to make the weight on both sides equal.

Thus, $50 = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''' + l$ mg.

The weighing is then repeated, placing the 50 gram weight on the right-hand pan and the other weights on the other pan. The weights then are placed thus:

$$20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''' + r \text{ mg.} = 50.$$

This double weighing gives us the ratio of the lengths of the balance arms.

$$\frac{\mathrm{R}}{\mathrm{L}} = 1 + \frac{l - r}{100000},$$

and also

$$50 = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''' + \tfrac{1}{2}(r + l) \text{ mg.};$$

if, for example, $r = 1{\cdot}8$ mg. and $l = 2{\cdot}5$ mg., then

$$50 = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''' + 2{\cdot}15 \text{ mg.},$$

and the ratio of the balance arms is

$$\frac{\mathrm{R}}{\mathrm{L}} = 1{\cdot}0000070.$$

In the same way the 20 gram weight is compared with the 10′ and 10″ weights, the 10′ with 10″, the 10′ with the 5, 2, 1′, 1″ and 1‴, and so on until all the brass weights have been compared. The ratio of the length of the arms should be determined in each case. In this way a series of equations will be obtained which may be written thus:

$$\begin{aligned}
50&=20+10'+10''+5+2+1'+1''+1'''+\mathsf{A}\\
20&=10'+10'' \qquad\qquad\qquad\qquad\qquad\quad +\mathsf{B}\\
10''&=10' \qquad\qquad\qquad\qquad\qquad\qquad\qquad +\mathsf{C}\\
5+2+1'+1''+1'''&=10' \qquad\qquad\qquad\qquad\qquad\qquad\qquad +\mathsf{D}
\end{aligned}$$

where A, B, C and D represent the amounts by which the one side exceeds the other, and consequently may be either positive or negative in the equations. If a standard weight is available, it may now be used to get the values of the other weights. But when, as is generally the case, a standard weight is not available, it is usual to assume that the sum of the whole of the weights is correct, *i.e.*

$$50+20+10'+10''+5+2+1'+1''+1'''=100 \text{ grams.}$$

If now we substitute in this expression the values of the various pieces in terms of any one piece, say 10′, we obtain

$$100 \text{ grams}=10\times 10'+(\mathsf{A}+2\mathsf{B}+4\mathsf{C}+2\mathsf{D}).$$

That is, the error on the 10′ piece is given by

$$\mathsf{S}=\tfrac{1}{10}(100-10\times 10')=\tfrac{1}{10}(\mathsf{A}+2\mathsf{B}+4\mathsf{C}+2\mathsf{D}),$$

in this way the following values for the pieces are obtained, viz.

$$\begin{aligned}
10'&=10 \text{ grams}-\mathsf{S},\\
10''&=10 \text{ grams}-\mathsf{S}+\mathsf{C},\\
5+2+1'+1''+1'''&=10 \text{ grams}-\mathsf{S}+\mathsf{D},\\
20&=20 \text{ grams}-2\mathsf{S}+\mathsf{B}+\mathsf{C},\\
50&=50 \text{ grams}-5\mathsf{S}+\mathsf{A}+\mathsf{B}+2\mathsf{C}+\mathsf{D}\\
&=50 \text{ grams}+\frac{\mathsf{A}}{2}.
\end{aligned}$$

The smaller weights are treated similarly, using the determined value of 10′ as the starting point in the calculation. When the whole of the pieces have been corrected in the above manner, we have a set of weights, the pieces of which are correct among themselves, and satisfactory for all purposes except absolute determinations. Should such determinations be required, it is usual to compare one piece of the set with a standard weight, and calculate the absolute weights of the other pieces from it.

Correction to Vacuum Standard

A few physical determinations, such as the density and absolute weight of a gas, require that the weight obtained should be reduced to vacuum standard. When a body is weighed in air it always weighs less than its true weight, by an amount equal to the weight of the air it displaces. This is due to the buoyancy of the air.

If V c.c. represents the volume of the object weighed, and d the weight of one cubic centimetre of air, then the weight of the air displaced is $\mathsf{V}d$ grams, and the real weight of the object is $\mathsf{W}+\mathsf{V}d$, where W represents the apparent weight. The volume of the object weighed is obtained by dividing the apparent weight by its density.

Hence we have the expression

$$\text{True weight} = \mathsf{W} + \frac{\mathsf{W}}{\mathsf{S}} \times 0{\cdot}0012 = \mathsf{W}\left(1 + \frac{0{\cdot}0012}{\mathsf{S}}\right),$$

where S is the density of the substance, and 0·0012 the weight of 1 c.c. of air under average atmospheric conditions. A similar correction must be applied for the effect of the buoyancy of the air on the weights. If S' be the density of the weights, then an amount $\frac{0{\cdot}0012}{\mathsf{S}'}.\mathsf{W}$ must be subtracted from the quantity above.

The true weight then becomes

$$\mathsf{w}\left(1+\frac{0{\cdot}0012}{\mathsf{s}}\right)-\mathsf{w}\left(\frac{0{\cdot}0012}{\mathsf{s}'}\right),$$

$$\text{or}\quad \mathsf{w}\left(1+\frac{0{\cdot}0012}{\mathsf{s}}-\frac{0{\cdot}0012}{\mathsf{s}'}\right).$$

The brass weights generally used have a density of 8·5, so that the final expression becomes

$$\mathsf{w}\left(1+\frac{0{\cdot}0012}{\mathsf{s}}-0{\cdot}00014\right)\text{ grams.}$$

In very accurate determinations the weight is reduced to the value it would have at a standard latitude, viz. 45°, and also to sea level. The reader is referred to text-books on Physics for the expressions used in this reduction.

2. Determination of Volume

The volume of liquids is determined by means of flasks, burettes, and pipettes, which are graduated to hold or deliver, as the case may be, definite volumes of liquids. Such apparatus, although sold as having definite capacity, should always be calibrated before use. To determine the volume of any given piece of apparatus it is usual to weigh the amount of water required to fill it up to the mark. In the case of the smaller measuring vessels mercury should be used instead of water. The weight should then be reduced to vacuum standard, and the volume of one gram of water at the given temperature be used to reduce the volume of the vessel to some standard temperature, generally 15°. Generally, however, this is not actually done, but the volume is obtained from tables which give the true volumes at various temperatures of given apparent weights of water. The tables are prepared from weights obtained by the use of brass weights in air under ordinary atmospheric conditions. For a table of such volume weight relations see Appendix, Table I.

It is preferable that mercury be used for calibrating small vessels, except in the case of vessels which have sharp angles. Mercury, having a density of 13·6, gives a much larger weight with a correspondingly smaller error.

If W is the weight of mercury required at a temperature $t°$ to fill a small flask of volume V, then for temperatures between 0° and 18° the volume is given by the expression

$$\mathsf{V}=0{\cdot}07351(1+0{\cdot}000182t)\mathsf{W}\ \text{c.cms.},$$

where 0·000182 is the mean coefficient of cubical expansion of mercury between 0° and 18°, and 0·07351 is its specific volume over the same range of temperature. A table giving the volume of an apparent gram of Mercury will be found in the Appendix (Table I.).

Calibration of Measuring Vessels

(*a*) *Measuring Flasks.* Measuring flasks are made to hold volumes of 1000 c.c., 500 c.c., 250 c.c., 200 c.c., 100 c.c., 50 c.c. and 25 c.c., and are provided with ground glass stoppers which fit into long, fairly narrow necks. The graduation mark ought to be about one-third up the neck. To calibrate such a flask, it is thoroughly cleaned, dried and weighed. It is then filled to within 2 or 3 cm. of the graduation mark with distilled water, and allowed to stand in the balance room for about half an hour, so that it may acquire the temperature of the surroundings. It is then carefully filled to the mark, so that the under side of the meniscus and the mark coincide, and weighed. From the weight and temperature the volume can then be calculated by means of Table I. (Appendix). The larger flasks, viz. 1000 c.c., 500 c.c., 250 c.c. and 200 c.c., need only be weighed to the nearest centigram, the others to the nearest milligram. Should it be found that a flask is very inaccurate, it is wisest to regraduate it. This is done by gumming a strip of paper either above or below the original mark, as the volume is too small or too large, and weighing the water held in the flask up to the new mark. Then the volume between the two marks, which is obviously the difference of the two determined volumes, can be divided so as to give the position of the new graduation mark.

For example, suppose the original mark represents a volume of 201·5 c.c., and a second mark 4 cm. lower down the neck represents a volume of 199·5 c.c. Then the true volume, 200 c.c., will be represented by a mark

$$\frac{0{\cdot}5}{2{\cdot}0} \times 4 = 1 \text{ cm. above the lower mark.}$$

The flask should then be filled to this mark and reweighed to confirm the previous measurements.

(*b*) *Pipettes.* Pipettes are made having capacities of 100, 50, 25, 20, 10, 5, 2 and 1 c.c., and are designed and graduated either to deliver or withdraw the stated volumes of a liquid. Accurate work with pipettes depends upon several points which are not always observed.

1. The top and bottom stems of the pipette should be fairly narrow, about 2 mm. internal diameter is a good average size for pipettes up to 10 c.c. capacity and 3 – 3·5 mm. diameter for larger pipettes, the pipettes usually supplied have much wider stems.

2. They must be entirely free from grease; the presence of grease is ascertained by filling the pipette with water, and allowing it to empty itself in the normal way. If drops of water are left adhering to the sides of the pipette it is greasy and must be cleaned. Grease may

be removed from a pipette by filling it with a hot solution of chromic acid, made by adding concentrated sulphuric acid to a solution of potassium bichromate. Greasiness is prevented by keeping pipettes, when not in use, standing in a tall cylinder of the above solution.

3. Pipettes must always be allowed to deliver in the same manner. The best method is to hold the pipette almost vertically at the side of, but not touching, the vessel into which it is being emptied, so that the liquid runs against the side. When all the liquid has run out the pipette point is touched against the wall of the vessel. A pipette should never be blown into, since this tends to make it greasy, and the quantity of liquid blown out varies, depending on the time which is allowed to elapse before the blowing. A pipette should take about forty seconds to deliver its contents. If a pipette delivers too quickly, the point should be closed somewhat by holding it in a blowpipe flame for a few seconds.

To calibrate a pipette a narrow strip of gummed paper is attached vertically along the upper stem, and a mark made upon it in what is judged to be about the correct position. The pipette is then filled with distilled water up to this mark, and its contents delivered into a previously weighed stoppered bottle, and weighed. A second mark is then made on the paper strip, either above or below the original mark, as the first volume was too small or too large, and the weight of the volume of water contained up to the new mark is obtained. The true position is then calculated from the two volumes, as indicated above. The final position should always be verified by weighing the contents up to that mark, and in a properly calibrated pipette the volume should not differ from the nominal value by more than 0·05 per cent.

Should the pipette be required to withdraw a definite volume of liquid, the process of calibration differs slightly from the foregoing method. A stoppered bottle is filled with water and weighed, and the pipette to be calibrated is filled from the bottle. The residue is then weighed, and the difference in the weights of the water gives the withdrawal volume of the pipette. Two positions must be determined on the stem, as in the last case, and the true position calculated from them. In using pipettes for the withdrawal of a definite volume of a liquid, care should be taken that the point of the pipette is always immersed to the same depth. This ensures that the same amount of liquid always adheres to the outside of the pipette. It is useful to etch a mark on the lower stem at the position to which the pipette must be immersed. A pipette used for withdrawal must always be dried before use. This is best done by passing the pipette to and fro through a bunsen flame, and blowing a current of air through it the while from a bellows. Pipettes should never be dried by means of alcohol or ether, since these substances nearly always contain grease dissolved in them, which they leave in the pipette on evaporation.

Having found the correct positions of the graduation marks for a series of flasks and pipettes, the marks must be etched on to the glass. This is done by coating the glass and paper strip with a thin layer of paraffin wax, and then, with a sharp knife, cutting a ring through the wax at the correct height. Hydrofluoric acid is then applied to the cut by means of a pad of cotton wool; after a few minutes the excess of acid is washed away and the wax removed.

(*c*) *Burettes.* These instruments are constructed to contain 50 c.c. of a liquid, and are graduated in $\frac{1}{10}$ c.c., so that they can be used to deliver quantities of a liquid up to 50 c.c., measured to $\frac{1}{100}$ c.c. In addition to errors of graduation, there arises in the use of a burette an error of parallax, due to the eye being on a different level from that of the meniscus. Errors of parallax can be avoided by placing a small mirror at the back of the burette and taking the reading when the image of the eye and the meniscus are both just visible. Shellbach burettes are often used for avoiding errors of parallax. These burettes have a white vertical stripe running down the length of the back of the burette, and a narrower blue stripe runs down the centre of the white one. The height of the meniscus is very easily read, for the appearance of the blue stripe is similar to the diagram (Fig. 1), the point p being the level of the liquid.

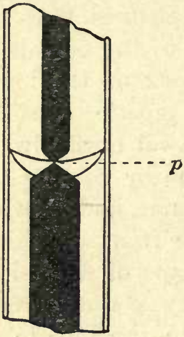

FIG. 1.

To calibrate a burette one may either run known volumes of water from the burette into a weighing bottle, and calculate the volumes from the weights, or what is far easier, use an Ostwald calibrating pipette (Fig. 2). This pipette, which has a volume of 2 c.c. between the marks a and b, is attached to the burette as indicated in Fig. 3.

The burette is then filled up to the zero mark with distilled water, and the pipette up to the mark a. The tap t is then carefully opened and the pipette slowly filled to the mark b, the tap is then closed and the height of the water in the burette noted. The pinchcock p is then opened and the liquid run from the pipette until the meniscus stands at a. The process is then repeated until the burette is empty. The volume of the calibrating pipette should always be checked by running two or three quantities of water into a stoppered weighing bottle, and weighing them. In this way we have the true volumes of various sections of the burette. These corrections are made use of by calculating the errors, and plotting them as ordinates against the burette readings as abscissae.

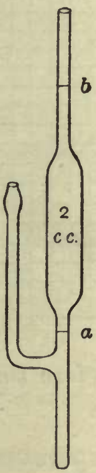

Fig. 2.

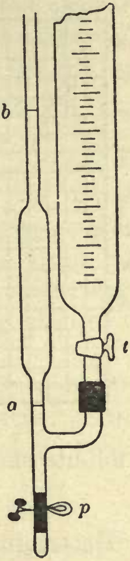

Fig. 3.

Thus, if we have the following readings of the burette:

1·96, 3·98, 5·98, 8·02, 10·03, 11·99, 14·00, 16·01

for a series of withdrawn quantities

2, 4, 6, 8, 10, 12, 14, 16,

then the errors are

+0·04, +0·02, +0·02, −0·02, −0·03, +0·01, ±0·00, −0·01,

which must be added to the burette readings to give the correct value. Fig. 4 represents a correction curve drawn from the values above. Having made a correction curve, the value for any reading can be obtained. Attention must be paid to the time of outflow of a burette; it should never be less than half a minute for 20 c.c., and about half a minute should elapse before the reading is taken.

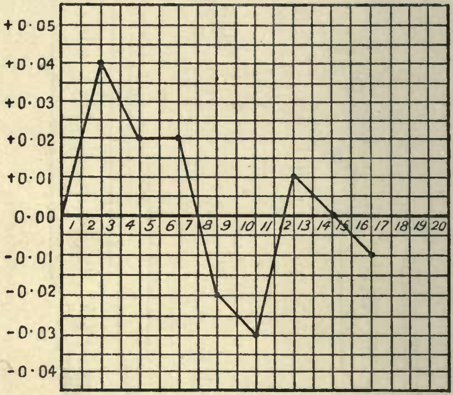

Fig. 4.

3. Determination of Temperature

Temperature is measured by means of thermometers, and of these there are four kinds. 1. Mercury thermometers (other liquids are occasionally substituted for mercury for special purposes); 2. Gas thermometers; 3 Resistance thermometers; and 4. Thermoelectric thermometers. Of the four varieties, mercury thermometers are in most general use, gas thermometers are rarely used and only for very special purposes, and the other two are used for determining very high and very low temperatures. The mercury thermometer can be used up to 350° under ordinary circumstances, but by filling the thermometer tube above the mercury with either nitrogen or carbon dioxide it may be used up to 550°.

A thermometer may be calibrated by one of two methods, either by comparison with a "normal" thermometer, or by determining a number of fixed points.

To calibrate a thermometer by comparison with a normal thermometer: the two thermometers are placed side by side in a liquid bath and the temperature of the bath slowly raised. The readings of the two thermometers are recorded every degree, and the errors plotted against the readings similarly to the method adopted for burettes. When thermometers are newly made they change the position of their zero relatively quickly, consequently it is advisable to determine the zero of a new thermometer periodically by immersing it in melting ice, and to correct all readings by addition or subtraction of the amount of change.

If the second method of calibration be adopted, the following list gives a series of fixed points which may be determined. The errors at these points are plotted against the readings as before.

Fixed Point.	Temperature.
Melting point of Ice, - - -	0°C.
Transition point of $Na_2CrO_4\,10H_2O$,	19°·85
,, ,, $Na_2SO_4\,10H_2O$, -	32°·38
,, ,, $NaBr\,2H_2O$, -	50°·37
,, ,, $SrCl_2\,6H_2O$, -	61°·0
,, ,, $Na_3PO_4\,12H_2O$, -	73°·4
,, ,, $Ba(OH)_2\,8H_2O$, -	77°·9
Boiling point of Water, - - -	100°·0 + 0·036 (P − 760)
,, ,, $SnCl_4$, - - -	114°·2 + 0·028 (P − 760)
,, ,, Aniline, - -	184°·2 + 0·051 (P − 760)
,, ,, Naphthalene, -	218°·1 + 0·058 (P − 760)
,, ,, Mercury, - -	357°·1 + 0·075 (P − 760)

where P represents the pressure in mm. under which the comparison is made. The transition points mentioned above are apparent melting points, and the temperature should be taken during the melting, the mass being constantly stirred.

It is not always possible to keep the whole of the mercury thread at the temperature of the bulb during a determination, some of the thread usually projects, and for an exact temperature a correction must be applied. If n is the number of degrees of the thread exposed, and β is the coefficient of apparent expansion of mercury, T the temperature determined, and t the mean temperature of the exposed thread, then the amount of the correction is given by

$$n\beta(\mathrm{T}-t).$$

Both the mean temperature and the coefficient of apparent expansion are difficult to obtain. As a rule 0°·01 is added for each division exposed for temperatures up to 100°, 0°·02 for temperatures between 100° and 200°, and 0°·07 for temperatures up to 500°.

Resistance Thermometers. These thermometers possess many advantages over mercury thermometers. They can be used over a very wide range of temperature, from $-245°$ to 1300°, with an accuracy of $\frac{1}{10}°$; they never change their zero point, and there is no exposed thread to correct for.

When metals are heated they change their resistance to an electric current regularly as the temperature is changed, hence it is obvious that if the rate of change be known, it is possible to use such metals to measure temperature. Experiment has shown that the resistance of pure platinum varies with the temperature according to the equation

$$\mathrm{R}_t=\mathrm{R}_0(1+\alpha t+\beta t^2),$$

where R_0 represents the resistance at 0°, and α and β are constants. It is obvious that if the value of R_t be determined at three temperatures, R_0, α and β will be known. Dewar and Fleming have shown that, at the absolute zero, the resistance of platinum is zero. Hence if two other well defined temperatures be chosen, *e.g.* the melting point of ice and the boiling point of water, and the resistance determined at them, all the data necessary for calculating α and β are known. The expressions are

$$R_{100} = R_0(1 + (100)\alpha + (100)^2\beta),$$
$$0 = R_{-273} = R_0(1 - (273)\alpha + (273)^2\beta).$$

The values of α and β are obtained by solving the above equations.

A curve can now be constructed, showing the relationship between temperature and resistance, by calculating the values of R_t by inserting different values of t in the general expression. The values of R_t are plotted as ordinates against the temperatures as abscissae.

A resistance thermometer consists of a length of very thin pure platinum wire, about a metre long, wound on a mica cross *a* (Fig. 5). The ends of the platinum are soldered on to thick copper leads *b*. The whole is contained in a glass or quartz tube *c*, which is fitted with a stopper *d* through which the leads pass. The stopper must be made of some material which will withstand the temperature to which it is to be subjected, *e.g.* asbestos.

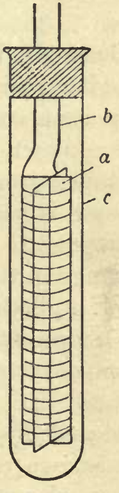

FIG. 5.

To make a measurement, the copper ends of the thermometer are connected to one arm of a Wheatstone bridge as indicated in Fig. 6. The thermometer is then immersed up to the stopper in the substance whose temperature is to be determined. After waiting for several minutes for the thermometer to take on the temperature, the resistance is measured.

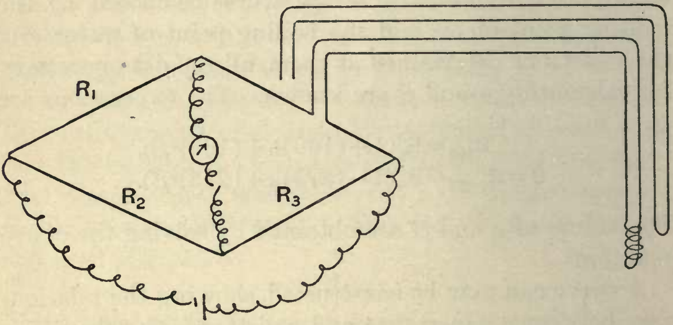

FIG. 6.

Alongside the leads of the resistance thermometer a similar pair of leads of the same wire are placed, these are connected at the end nearest the thermometer, and are known as the compensator. The resistance of the compensator is measured before and after the thermometer is placed in position. The object of this is to compensate for any change in the resistance due to change in the temperature of the leads.

If R_t is the resistance of the thermometer and leads at a temperature t, and R_1 and R_2 the resistance of the compensator before and after the thermometer has been placed in position, then the resistance R_t must be reduced by an amount $(R_2 - R_1)$ to give the correct resistance of the thermometer. The temperature can now be obtained from the resistance temperature curve.

Thermo-electric Thermometers or Thermocouples. If two metals be joined together at both ends to form a loop, and one joint of the loop be heated, an electric current will flow round the circuit in one or other direction, depending on the nature of the metals. The electromotive force of the current will depend upon the difference of temperature between the two joints. This principle has been made use of in thermo-electric thermometers. Two wires, of metals suitably chosen to withstand the temperatures to which they are to be exposed, are soldered together at one end and placed in a glass or silica tube. The free ends pass out at the end of the tube. Such an arrangement constitutes a thermo-electric thermometer. The two free ends are connected to one arm of a Wheatstone bridge, and the electromotive force determined when the couple is subjected to different temperatures. In these determinations it is all-important that the joints of the free ends of the couple with the bridge should be at the same temperature, and this temperature must be known, for the electromotive force depends on the difference of the temperatures of the junctions.

A couple must be calibrated, and a temperature electromotive force curve prepared, before it can be used. This is done by immersing it in substances of known temperature, and measuring the electromotive force for each temperature. The difference in temperature between the connections of the couple and the bridge, and the couple itself, are plotted as abscissae against the electromotive force as ordinates. It is usual in calibrating a couple to place the connection with the bridge in a constant temperature bath.

As fixed points, those given already under the description of mercury thermometers may be used, and in addition the following are reliable points for high and low temperatures:

Fixed Point.	Temperature.
Boiling point of Oxygen, - -	$-184°{\cdot}2+0{\cdot}051\,(P-760)$
Melting point of Ether, - - -	$-117°{\cdot}6$
„ „ Nitrous Oxide, -	$-102°{\cdot}3$
„ „ Sulphur Dioxide, -	$-72°{\cdot}7$
„ „ Mercury, - -	$-38°{\cdot}9$
„ „ Cadmium, - -	$+321°{\cdot}7$
Boiling point of Sulphur, - -	$+444°{\cdot}8+0{\cdot}088\,(P-760)$
Melting point of Antimony, - -	$+630°{\cdot}7$
„ „ Gold, - - -	$+1064°$

Thermocouples are manufactured provided with a voltmeter in which the usual scale is replaced by a temperature scale. This has been calibrated for the particular couple attached to it. Measurements by this type of instrument are not so accurate as those carried out as described above. Below is given a list of the couples in general use, together with maximum temperatures for which they may be employed.

Materials.	Maximum Temperature.
Platinum ; 10 % Platinum Iridium Alloy, -	1700°
Platinum ; 10 % Platinum Rhodium Alloy,	1700°
Constantan ; Iron, - - - - -	1000°
Constantan ; Copper, - - - -	850°
Bismuth ; Antimony, - - - -	250°

CHAPTER III

THERMOSTATS AND CONSTANT TEMPERATURE OVENS

THE results of most physical determinations are dependent on the temperature at which they have been obtained. Consequently, it is necessary to maintain a steady temperature during the whole of the experiment, or at least during that part of it which is influenced by temperature. Constant temperatures are obtained by surrounding the vessels in which an experiment is being conducted, with some liquid or vapour whose temperature is known and constant. Such constant temperature baths are termed thermostats, and for our purpose may be divided into two groups: (1) Those capable of furnishing a constant temperature for a comparatively short period, and (2) those which maintain a constant temperature for an indefinitely long period.

1. **Thermostats for Short Periods.** The simplest and crudest form of thermostat consists of a large beaker or metal vessel filled with water, whose temperature is kept about the required point by a bunsen burner which is regulated by hand to keep the temperature at the required point. A stirrer is placed in the vessel, and by constant stirring and careful regulation of the heating, a moderately constant temperature may be maintained for two or three hours. In many cases it is only necessary

to keep the temperature constant, the actual temperature, so long as it is known, being immaterial. Such a temperature may generally be obtained by using a large vessel of water which has stood in the room for some hours, it will generally have a temperature slightly below that of the room, but it will not vary much in the course of an hour or two. In the case of low temperatures, *e.g.* 0°, a constant temperature may be obtained by packing crushed ice round the experimental vessels, and leading away the water as quickly as it is formed by the melting ice. Other low temperatures can be obtained by placing the experimental vessels in a metal box which is surrounded by a concentrated solution of a salt which forms a cryohydrate. This box in its turn is surrounded by some cooling agent, which will produce a slightly lower temperature than the cryohydric temperature of the salt in the inner box. The effect of the outer cooling is to lower the temperature of the solution in the inner box to the cryohydric point, where it remains stationary until all has solidified, thus cooling and maintaining the experimental vessels at the cryohydric temperature. Below are given a few salts, together with their cryohydric temperatures, which may be used for this purpose.

Salt.	Cryohydric Temperature.
Sodium Chloride, - -	$-22°$
Ammonium Sulphate, -	$-17°$
Potassium Chloride, - -	$-11°$
Potassium Nitrate, - -	$-3°$

For high temperatures, good results may be obtained by using the vapours of liquids at their boiling points.

Such temperatures, it is true, depend on the barometric height, but for experiments lasting only a few hours this is unlikely to occasion any serious difficulty. A thermostat of this type may be made of either metal, glass or porcelain, as indicated in Fig. 7, fitted with a condenser **C**. The inside vessel **A** is filled with water or some other liquid depending on the temperature required, and this is heated by the vapour of the liquid in the outer vessel **B**. The experimental vessels and substances are placed in the liquid in the vessel **A**, and so kept at a constant temperature.

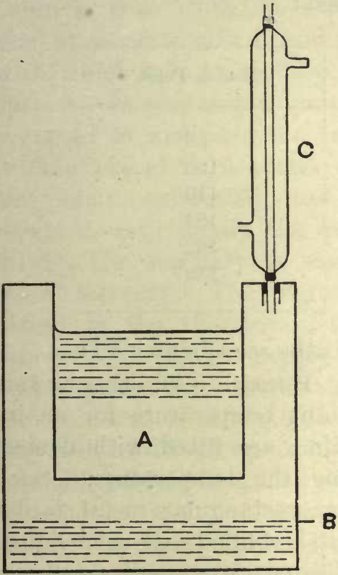

Fig. 7.

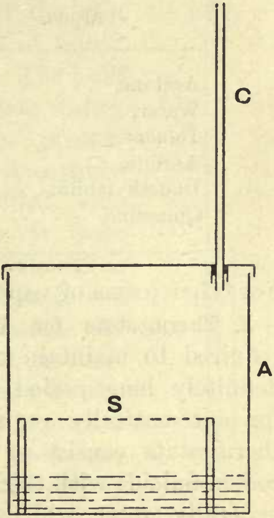

Fig. 8.

Another arrangement, depicted in Fig. 8, may be used when water or high boiling non-inflammable substances are used for heating. In this, the experimental vessels are placed directly in the vapour itself, care being taken that they do not stand in such a position that the liquid from the condenser **C** falls upon them. **S** is a perforated shelf on which the vessels may be placed.

For thermostats of the types mentioned above, the following liquids may be used:

Liquid.	Boiling Point.
Acetone, - - -	56°
Water, - - -	100°
Toluene, - - -	110°
Aniline, - - -	184°
Dimethylaniline, - -	192°
Quinoline, - - -	239°

For other forms of vapour baths see Chapter VII.

2. **Thermostats for Long Periods.** All thermostats required to maintain constant temperature for an indefinitely long period of time are fitted with devices for automatically regulating the temperature. Such thermostats consist of large rectangular metal tanks, coated outside with thick felt, and filled with some liquid, generally water, which is heated by a small gas flame, whose height is automatically regulated.

A useful form of temperature regulator is illustrated in Fig. 9. It consists of a large glass bulb **A**, connected to a stout-walled capillary tube **B**, which is in its turn connected to a wider tube **C**, at its upper end. This wider tube has a side tube **D**, and is fitted with a rubber stopper, through which is placed a glass tube **E**, drawn out to a capillary. A tiny pinhole **F** is pierced in the wide part of **E**. The bulb **EA** is filled with a liquid of fairly large coefficient of expansion, *e.g.* paraffin oil, toluene, or a 20 per cent. solution of calcium chloride in water. To fill A, the side tube D is closed with a piece of rubber tubing and a clip, C is then connected to a water-pump and the apparatus exhausted. The tube connecting C to the pump is then closed by a pinchcock, and that attached to D is dipped into the liquid with which A is to be filled, and the clip opened. In this way a quantity of liquid is caused to rush into the bulb. The bulb is then placed in a vessel of hot water, and again exhausted, and the process repeated, until finally the bulb is entirely filled. The capillary is then filled with clean mercury. The regulator is now placed in the thermostat, the tube E is connected to the gas supply, and D to the burner placed beneath the thermostat. As the temperature of the bath rises, the mercury will be driven up the capillary by the expanding liquid in A, until finally it reaches the end of E and closes the main gas supply. A small flame is maintained by the gas coming through the tiny hole F. As the bath cools down the mercury recedes, and the end of E is opened again, and the flame increases in size again. The position of the tube E, and the amount of mercury in C, must now be so regulated that E is just closed at the required temperature, *i.e.* the main gas supply is cut off when the water of the bath has reached the desired temperature. There are numerous varieties of temperature regulator, but as the principle involved is the same as that just described, it seems unnecessary to describe them individually here.

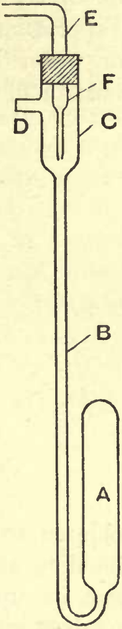

FIG. 9.

Should the thermostat be arranged for temperatures above 50°, it is necessary to have some arrangement for constantly adding water to compensate for the loss by evaporation. The well-known constant-level device used for water baths is quite suitable for this purpose. It consists of a wide metal tube A (Fig. 10), which is soldered to the side of the thermostat, as indicated in the diagram. A narrower tube B is fitted into A, so that its upper end is level with the height of water required in the thermostat. The lower end of B is connected to the waste pipe. Water enters the apparatus by the side tube C, and should the level of the water in the thermostat be below that of the tube B, then water will enter the thermostat until the heights are adjusted, and then the stream from the tap will flow away by means of B.

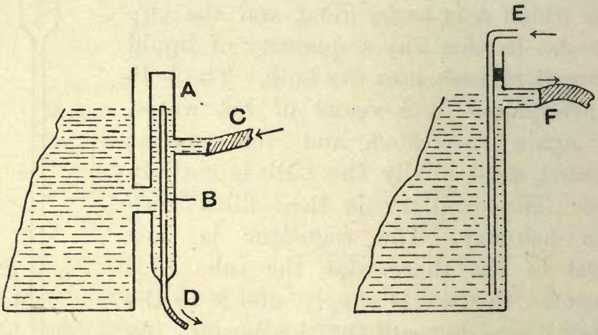

FIG. 10.

A much simpler device will, however, keep the level constant. This consists of a metal tube E (Fig. 10), soldered to the inside of the thermostat, and an outlet tube F placed at the maximum level height. This arrangement serves other purposes than the one just mentioned. In the summer months, when working at temperatures between 15°–25°, the atmospheric temperature often exceeds that required in the thermostat, so that the temperature regulator is rendered ineffective. Under such circumstances it is usual to lead in a stream of cold water. This can be done by the constant level arrangement above, and if the flame be left burning below the thermostat, and the stream be not too rapid, the combined heating and cooling will, with a good temperature regulator, just balance and keep the thermostat correct. This is particularly useful in summer, for often the temperature of the atmosphere falls at night, and with this double arrangement of heating and cooling the temperature will be kept constant.

Despite all temperature regulators, the thermostat will be useless unless constantly stirred. For this purpose numerous propeller-like stirrers have been devised, which are driven either as in **A** (Fig. 11), by a light vane whose motive power is a tiny flame, or by a motor as in type **B**.

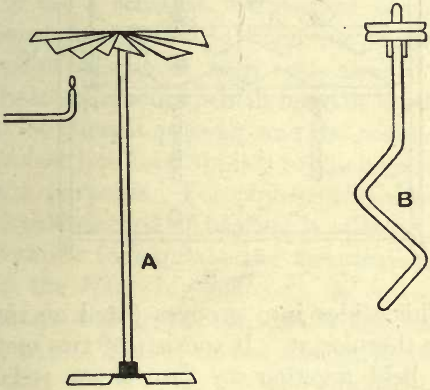

Fig. 11.

In very many determinations, liquids and solids require to be shaken at constant temperature for prolonged periods. This being the case, it is advisable that the thermostat should be fitted up with an arrangement for shaking, which will at the same time serve as a very efficient stirrer. Fig. 12 illustrates a useful rotary shaker. This slides into grooves fitted on two parallel sides of the thermostat. It consists of two metal bars A, which are held together by two brass rods D. This framework just fits into the grooves on the sides of the thermostat, and carries an axle K. To one end of the axle a pulley H is attached, and on either side of it are brass plates, cut into which are deep V-shaped notches. To each pair of notches, a wooden clamp W, actuated by

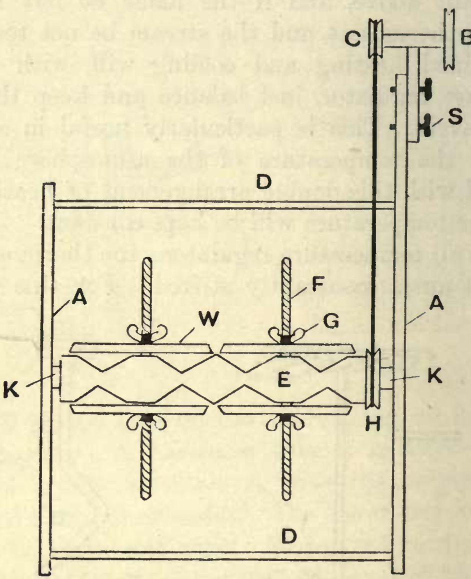

FIG. 12.

a thumbscrew FG, is attached. These serve to hold the bottles and flasks which are to be shaken. The axle and shaking arrangement are rotated by a belt passing round the pulleys H and C. The pulley C is fixed on the same axle as a second pulley B, which is directly driven from a motor. The two screws S represent an arrangement for changing the distance between C and H, and are extremely useful for tightening the belt when it has worked slack.

A thermostat fitted up in the above way will give a temperature which does not fluctuate more than $\frac{1}{10}$°, but generally it may not be used above 100° C. If, however, water be substituted by a concentrated calcium chloride solution, it may be used for temperatures up to 150°. Temperatures higher than this are rarely, if ever, required for long periods, and if they are, then it is advisable to use a constant temperature oven.

High Temperature Ovens. When an electric current passes through a wire of high resistance, it raises the temperature to an amount which may be determined by the amount of current passing, and the resistance of the wire. This fact has been applied to the heating of ovens for chemical purposes. For physico-chemical purposes, however, if this method of heating is to be of any use, it must be possible to regulate the temperature. This is achieved in the following manner: A coil of wire of high resistance A (Fig. 13) constitutes the heating part of the apparatus. This is wound round the oven, which may be of any shape from a long cylindrical tube to a rectangular box. [In the figure it is represented by a rectangular box B.] The wire must be insulated with respect to its several coils, it is therefore usual to surround the oven with asbestos before the wire is wound on. The wire is then enclosed by a second metal box, which is similarly coated with asbestos to prevent excessive loss of heat. A temperature regulator **C** is fitted into the box. This differs from the regulator described before, in being entirely filled with mercury, it is in fact a thermometer which has a large bulb. A platinum wire **L** is fused through the bulb of the regulator to make electrical contact with the mercury. A stout platinum wire **M** passes through the cork at the top of the regulator. The two wires **M** and **L** are connected through

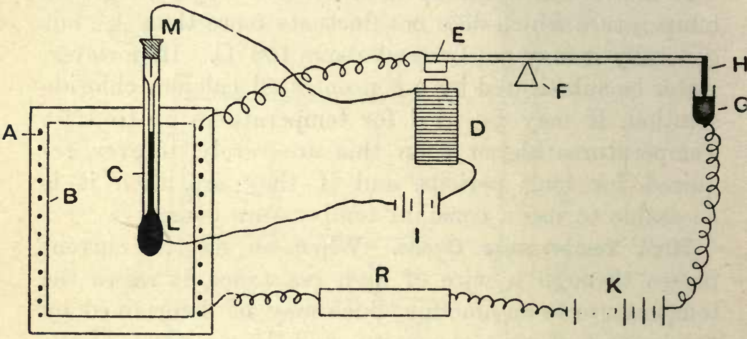

FIG. 13.

a small battery of 2-3 accumulator cells with a small electromagnet **D**, as shown in the diagram. The heating coil **A** is connected through a variable resistance with a large battery, or with some other source of current. The circuit is completed by way of the cup of mercury **G**, a thick platinum point **H** and the lever **EH**, as indicated in the diagram. The level is suspended on a fulcrum **F**, and carries a small piece of soft iron **E** at one end, and in its normal position lies so that the platinum point **H** is immersed in the mercury. When the current is switched on, and the oven begins to heat up, the mercury in the regulator expands and rises in the capillary tube, until it finally touches the platinum wire **M**. When this happens the electromagnet circuit is complete, and the soft iron **E** is drawn down to the magnet core. This withdraws the platinum point **H** from the mercury in **G** and thus breaks the main circuit, thereby cutting off the heat supply from the oven. When the temperature has fallen a little, the mercury recedes in the regulator, and the electromagnet circuit is broken, thus releasing **E** and again completing the main circuit. Any definite temperature may be obtained in the oven by adjusting the amount of mercury in **C** and by regulating the position of **M**. An arrangement such as that described is suitable for temperatures up to 350°. For higher temperatures a rod of metal may be used as regulator, which by its expansion sets the magnet in action in a way similar to the mercury regulator.

Electric heating can obviously be adapted to water thermostats. The arrangement is practically the same as that described above, the ordinary toluene regulator may be used, but the lower electrical connection is made through the stem and not through the bulb. The heating wire is placed round the bottom of the thermostat on the inside, and insulated from the metal by a number of porcelain studs which are cemented to the bottom.

CHAPTER IV

MANIPULATION OF GASES

BEFORE proceeding to the description of methods for determining the density of gases, it will be well to consider briefly their manipulation. The first essential in the determination of the density of a gas is that it should be pure and dry. The question of the purity of gases cannot be dealt with here; information on this subject must be sought in works of reference on Chemistry. A few remarks, however, on the drying of gases may not be entirely out of place. A gas is most effectually dried by passing it through concentrated sulphuric acid followed by a considerable length of phosphorus pentoxide. These substances must obviously not be used for gases which react with them; they may be used for most of the commoner gases, the chief exceptions being ammonia, nitric oxide and sulphuretted hydrogen. Ammonia should be dried by passing it slowly through a long tube of quicklime, or barium oxide. Nitric oxide and sulphuretted hydrogen are usually dried by liquefying and then distilling off the gas from the moisture. The pure gas having been obtained, it has next to be introduced into an evacuated bulb, in which it is weighed. The bulb is exhausted, and the gas introduced by means of one of the many mercury pumps. Of these the one best suited to our purpose is the Toepler pump, which is comparatively simple in construction, and easily operated.

Toepler Mercury Pump. The pump consists of a cylindrical chamber or barrel A (Fig. 14), which is about 20 cm. long and about 5 cm. diameter. The ends of the barrel are tapered down to about 1·8 cm. diameter, and the narrowed ends are joined by a tube B of about 1·5 cm. diameter. The joints between A and B must be made as acute-angled as possible, otherwise there will be great danger of breaking the pump when it is in operation. A narrower side tube C is attached to B, this carries a glass valve D, and is connected to a drying tube E which is filled with phosphorus pentoxide, and closed by a well-fitting three-way tap F. A stout-walled capillary tube G is attached to the top of the pump chamber, this should be about 80 cm. long, and bent at its lower end as indicated, so that any gas expelled from the pump may be collected. A tube J, about 80 cm. long and 1·3 cm. diameter, is attached to the lower end of the pump barrel; this tube is made long so that, when the pump is evacuated, the mercury will always stand below the junction of B with

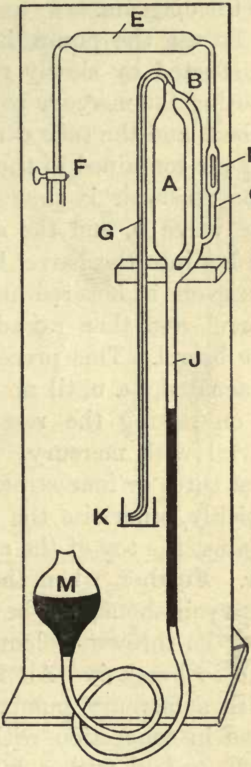

FIG. 14.

the barrel. The capillary **G** dips into a small stout-walled dish **K** containing mercury, and the end of **J** is connected by a piece of thick-walled rubber pressure tubing, 150 cm. long, with a mercury reservoir **M**. The whole is attached to a suitable wooden stand, as indicated in the diagram.

To use the pump, it should first be evacuated; this is effected by slowly raising the reservoir and thereby causing the mercury to rise and fill the barrel **A**, the side tube **B** and the tube **C** up to the valve. This will expel the air contained in those parts by way of the capillary. The reservoir is then cautiously lowered; this releases the valve **D**, and the air contained in the drying tube rushes into the barrel by way of the side tube **B**. The reservoir is lowered until there is no mercury in the barrel, and then raised again to expel the contents of the barrel. This process is repeated until the pump is evacuated, *i.e.* until no bubbles of air are expelled from **G** on raising the reservoir and completely filling the barrel with mercury. Care must be taken during the first three or four strokes not to lower the reservoir too quickly, otherwise the mercury may be driven violently against the top of the evacuated barrel by the incoming air. Further, when the pump is nearly exhausted, the reservoir should not be raised too rapidly, or the mercury may be thrown violently against the top of the barrel and so break it. All taps and ground joints connected with a mercury pump, and, indeed, with all apparatus used in connection with work on gases, should be kept well greased with a lubricant which is absolutely non-volatile, and which does not react in any way with the gases it comes in contact with. Such a lubricant is the one proposed and used by Ramsay. It is made by heating together on a sandbath a mixture of twenty parts of soft indiarubber, ten parts of vaseline and one and a half parts of hard paraffin wax. The mass must be constantly stirred until it is homogeneous, it will then keep indefinitely.

An improved and simplified form of Toepler pump has recently been described by A. von Anthropoff (*Chem. Zeit.* 1910, 34, 979). This pump differs from the older form chiefly in the design of the barrel and the side tubes connected to the barrel. Fig. 15 illustrates the portion of the pump which has been changed. The barrel **A** is placed at an angle of 45° to the tube by which the mercury enters, and also to the tube carrying the valve **B**. The side tube connecting the top and bottom of the barrel has been done away with. The special advantage in this pump is that it is not so liable to breakage as the other form. As will be seen from the diagram, it is impossible for mercury to be thrown violently against the top of the pump, at the worst it can only hit the side of the barrel, and here the blow is not a direct one. Further, there are fewer joints, and the intermediary tube, which is the great weakness in the original Toepler pump, is not present at all.

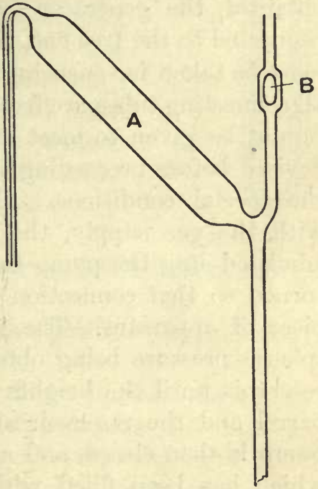

FIG. 15.

To exhaust a bulb or other piece of apparatus, it is connnected to one of the tubes of the three-way tap, either by fusing the tubes together, or by means of a piece of thick-walled rubber tubing which is well wired on. If the latter method be adopted, the two glass tubes must be brought together so that they touch. Having attached the apparatus, the tap is opened so that there is connection with the interior of the pump, and the process of evacuation proceeds as already indicated. The apparatus may now be filled with gas while still attached to the pump. If the gas is easily obtained, the generator or gas-holder may be directly connected to the free end of the pump tap. Precautions must be taken for ensuring that the gas is dry, and that all connecting tubes are free from air. General directions cannot be given to meet every case, and they must be devised before proceeding with the experiment, to meet the special conditions. Having connected the pump with the gas supply, the tap is opened, and the gas admitted into the pump barrel. The stop-cock is then turned so that connection is made with the exhausted piece of apparatus. The gas will rush into it, atmospheric pressure being obtained by raising the mercury reservoir until the heights of the mercury in the pump barrel and the reservoir are the same. The tap of the pump is then closed, and also the tap of the apparatus which has been filled with gas. The apparatus may then be detached from the pump and weighed.

If the gas to be examined can only be obtained in small quantities, and is contained in a small tube standing over mercury, it may be introduced into the pump by fusing on to the free tube of the pump tap a piece of stout capillary tubing bent as in Fig. 16. The end of this tube is drawn out to a point and sealed. The tube is then exhausted and placed in a deep mercury trough, and the tube containing the gas is brought over it. Then the capillary is raised until it reaches the top of the tube, and its point is broken off by pressing it against the side. The tap is then opened, and the gas enters the pump, followed by mercury, which is allowed to enter until the stopcock is passed. The gas can now be driven into an exhausted bulb as described above.

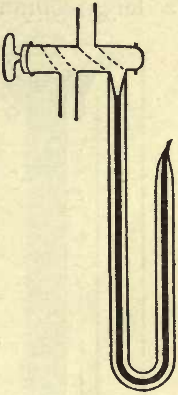

FIG. 16.

Purification of Mercury. It is important in working with pumps and gases, that the mercury used should be pure and dry, otherwise it will leave a "tail" which will dirty the pump and may affect the gases which come in contact with it. For the purpose of purification we may divide the impurities of mercury into two groups:

(i) Metals which are more electro-positive than mercury, *e.g.* Zinc, Iron, Copper, etc.

(ii) Metals which are less electro-positive than mercury, *e.g.* Gold.

1. *Removal of Metals more electro-positive than Mercury.* One of the simplest methods for the removal of these impurities is to place the mercury in a wide Drechsel bottle, cover it with a solution of mercurous nitrate containing a few drops of nitric acid, and draw a current of air through for several hours, by means of a water pump.

Equally effective and simple is the method which consists in placing about 250 grams of mercury in a stoppered bottle with a little mercurous nitrate, and shaking in a mechanical shaker for several hours. The stopper of the flask must be well wired on in this method of treatment.

When the mercury has been treated by one of the former methods, or if it is not very impure, it may be obtained quite pure by allowing it to run down a long column of mercurous nitrate solution. The apparatus for this treatment consists of a long wide tube A (Fig. 17), to whose lower end a capillary tube of 1 mm. bore, and bent as in the diagram, is attached. The tube is mounted on a wooden stand, and a funnel B, which is drawn out to a fine point, is placed at the top of the tube. The funnel causes the mercury to flow in a fine stream of drops. By this method the mercury flows from the capillary pure and dry.

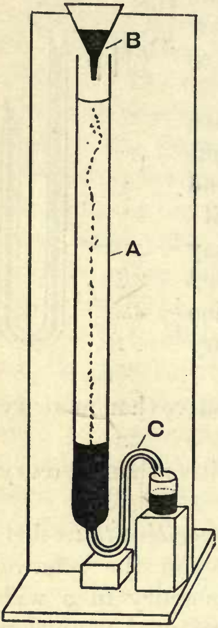

Fig. 17.

2. *Removal of Metals less electro-positive than Mercury.* Metals which are less electro-positive than mercury can only be removed by distilling the mercury; this, under ordinary circumstances, is a very disagreeable process. Dunstan and Dymond (*Phil. Mag.* 1890, p. 367) have, however, described a piece of apparatus by means of which mercury can easily and safely be distilled in a Toricellian vacuum.

The apparatus consists of a Jena glass tube 750 mm. long, and 1·5 cm. wide, A (Fig. 18). At the top of this tube a stout bulb B, of 500 c.c. capacity, is blown. This tube is filled with mercury and stands in a glass trough C, to such a depth that the bulb is half filled with mercury. A capillary tube D, also filled with mercury, passes through a rubber stopper E in the bottom of the mercury trough, and right up the tube **B**, so that about 3 cm. project into the bulb **A**. The capillary tube is bent as indicated in the figure. The bulb **A** is surrounded by a ring burner **F**, and protected from the direct action of the flame by a cone of asbestos **G**; it is also covered by a layer of asbestos. When the bulb is heated, the mercury evaporates quietly under the reduced pressure, and passes down the capillary, from which it drips into the bottle **K**. Fresh mercury for distillation is added to the trough **C**. The mercury used for distillation must be dry, free from metals more electro-positive than mercury, and from solid impurities. Some of the metals more electro-positive than mercury, *e.g.* zinc, are distinctly volatile, consequently distillation would not effect a purification. Mercury may be freed from solid impurities by filtering it through chamois, or through a filter paper which has a tiny pinhole in its point. Moisture can best be removed from mercury by placing it in a steam oven for several hours.

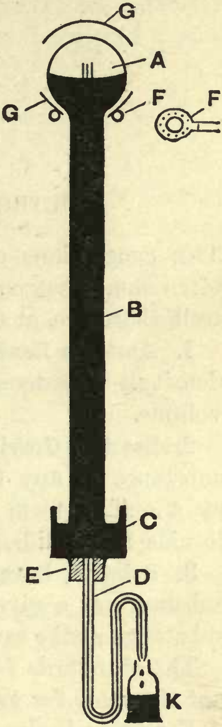

Fig. 18.

CHAPTER V

DETERMINATION OF DENSITY

THE conceptions of Density and Specific Gravity are often somewhat confused in their application, it will be well, therefore, at the outset to define these quantities.

1. **Absolute Density,** this is generally known simply as density. The density of a substance is the mass of unit volume.

2. **Specific Gravity** is the ratio of the density of a substance at any temperature to the density of water at 4°. The term specific gravity is only applied to liquids and solids.

3. **Relative Density** is the ratio of the density of a substance at a given temperature to that of a standard substance at the same temperature.

The standards for relative density determinations are not the same for gases as for liquids and solids.

For gases, hydrogen is the standard of relative density, although in many cases air is used. It is obviously incorrect to use a substance of variable composition as a standard, and consequently all relative gaseous density determinations should be made with hydrogen as the unit. In making relative density determinations of gases, it is essential that the pressure of the gas and the standard of comparison should be the same. It is not necessary that this should be the normal pressure, *i.e.*

760 mm. of mercury, for under moderate pressure changes all gases are equally affected.

The standard used for determining the relative density of liquids is water, so that the relative density of a solid or liquid at t° may be expressed by

$$\frac{\text{The density of the substance at } t^\circ}{\text{The density of water at } t^\circ}.$$

In physical chemistry we often express our density determinations in functions of the density, *e.g.* Specific Volume, Atomic Volume, and Molecular Volume.

The Specific Volume is the volume occupied by unit weight of a substance, *i.e.* it is the reciprocal of the specific gravity.

Molecular Volume is the volume occupied by the molecular weight of a substance in grams.

Atomic Volume is the volume occupied by the atomic weight of an element in grams.

Thus, if d be the specific gravity, v the specific volume, m the molecular volume, a the atomic volume, A the atomic weight, and M the molecular weight of an element, the following expressions give, in equation form, the relationships of the various factors:

$$d = \frac{1}{v}, \quad v\mathsf{A} = a, \quad v\mathsf{M} = m.$$

In recording a density determination it is usual to express the temperature at which it has been determined, and in the case of relative density and specific gravity, the standard from which it has been obtained. Thus, for solids and liquids, D_4^{25} indicates that the specific gravity was measured at 25° and the standard was water at 4°; for gases $\mathsf{D}(\mathrm{H}=1)$ means that hydrogen was the standard in this case. The densities of gases are always obtained from volumes reduced to normal conditions, *i.e.* 0° and 760 mm.

1. Density of Solids

In this section only those methods will be considered which are in general use for chemical purposes, for a description of other methods, the student is referred to text books on Mechanics.

The volume of a solid is never determined by measurement of its axial dimensions, for it is only very rarely that the form of a solid is sufficiently simple and regular to allow of even a moderately accurate computation of its volume being made by this method.

The volume of a solid is determined by measuring either the weight or the volume of a liquid displaced by it.

Before proceeding to determine the volume of a solid, it must be carefully examined to see that there is neither air bubbles nor "mother liquor" locked in the interior. Should these be found, it must be powdered and, in the case of the presence of "mother liquor," pressed between filter papers and then left to stand in the air for several hours.

(i) **Burette Method.** The simplest method of determining the density of a solid is to place a small weighed portion of the substance into a burette containing a measured quantity of a liquid, which neither dissolves nor has any action on the solid substance. The liquid will then give a different reading on the burette scale. The difference between the initial and final burette readings gives the volume of the solid.

If W is the weight of the substance and v its volume, then

$$\frac{\mathsf{W}}{v} = \text{density.}$$

(ii) **Specific Gravity Bottle Method.** A second method, useful for finely powdered substances and small crystals, entails the use of a specific gravity bottle. This is a wide-necked bottle, shaped as in Fig. 19, fitted with a perforated stopper *s*, and having a capacity of 50 c.c. or 25 c.c. The bottle is carefully cleaned and filled with freshly boiled distilled water, or other liquid if water is unsuitable for the determination. The stopper is then inserted, taking care that no strain is produced in the glass and that no air bubbles remain. The bottle is then dried and placed in the balance case, and after standing there for half an hour it is weighed. A known weight of the substance whose density is to be determined is now placed in the bottle. The stopper is again inserted and the bottle re-weighed. When adding the solid, great care must be taken to remove all air bubbles which may be adhering to it. This is best carried out by placing the bottle in boiling water as long as bubbles are given off, then it is removed, cooled, and completely filled with the liquid. The stopper is inserted as before, and the bottle allowed to stand for about an hour in the balance case, and re-weighed.

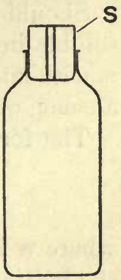

FIG. 19.

If W is the weight of the solid, W' the weight of the bottle filled with water, and W'' the weight of the bottle containing water and solid, then

$$\text{the relative density} = \frac{W}{W + W' - W''}.$$

For most purposes this expression gives a result accurate enough for the required object, but for more exact work the value must be reduced to water at 4° and vacuum standard.

If N is the density of water at the temperature of the experiment $t°$, and 0·0012 the mean density of air, then the corrected expression is

$$\text{Density} = \frac{W}{W + W' - W''}(N - 0{\cdot}0012) + 0{\cdot}0012.$$

Should the substance to be measured react with, or be soluble in water, then a liquid of known density which is without action on the solid must be chosen, *e.g.* benzene, alcohol, or aniline.

The formula for calculating the density then becomes

$$\text{Density} = \frac{Wd}{(W + W' - W'')},$$

where W is the weight of the substance, W' the weight of the bottle and liquid, W'' the weight of the bottle, liquid and solid, and d the density of the liquid.

(iii) **Method of Floating Substances.** Neither of the above-mentioned methods entirely removes the possibility of error arising from contained air and mother liquor, and since these impurities can only make a solid specifically lighter, the following method almost entirely eliminates errors of this nature.

A wide-necked tap funnel is cleaned, dried and about half filled with a dense liquid which has no action on the substance to be determined, and in which the substance will float. Then a number of carefully chosen crystals or pieces of the substance are added to it; they will all float on the surface. A second liquid of density less than that of the solid, and which mixes with the first liquid, is slowly added and well shaken, so that a homogeneous liquid is obtained. After one or two additions, several of the crystals will slowly sink, *i.e.* their density is slightly greater than the density of the liquid mixture. The heavier liquid is then added drop by drop, until the densest and, consequently, the purest crystals just remain suspended in the liquid, *i.e.* they have the same density as the liquid. When this is the case the liquid is run off and its density is determined. For method see next section of this chapter.

The following liquids are suitable for this method of determination:

Liquid.	Density.
Methylene Iodide, - -	3·324
Bromoform, - - -	2·90
Methylene Bromide, - -	2·499
Ethylene Dibromide, -	2·18
Ethyl Iodide, - - -	1·93
Alcohol, - - - -	0·806
Benzene, - - - -	0·899
Ether, - - - -	0·736

EXPERIMENTS

(i) *Determine the Density of Calcspar.* Choose several crystals of calcspar of such a size that they will easily slip into a burette. Examine them with a lens, and discard those which contain bubbles of occluded gas. Weigh the crystals chosen, to the nearest milligram, and slip them into a burette half full of water, the height of which has been previously read. Measure the new height, and from the volume of the crystals thus determined, calculate the density.

(ii) *Determine the Density of Ferric Oxide.* Weigh a small specific gravity bottle full of distilled water. Then pour out half the contents and add an accurately weighed quantity (about 5 grams) of ferric oxide. Place the bottle and contents in a bath of boiling water until all adhering air bubbles have been expelled, cool, and completely fill the bottle with distilled water. Place in the balance case, and after it has stood for an hour, re-weigh. From the weighings calculate the density of ferric oxide (1) without corrections, (2) with corrections.

(iii) *Determine the density of Crystallised Copper Sulphate.* Examine a number of crystals of copper sulphate, and pick out about a dozen which appear to be quite homogeneous. Place them in a dry separating funnel of about 200 c.c. capacity, and pour on to them about 30 c.c. of bromoform. Then carefully add absolute alcohol in small quantities, shaking or stirring after each addition, until one or more of the crystals sink. Now add bromoform, with continued stirring or shaking, until the densest crystal just floats in the liquid. The liquid and crystals now have the same density. The liquid must now be run off, and its density determined at the same temperature as that at which the experiment has been carried out. The density of the liquid gives the density of the crystals.

2. Density of Liquids

For approximate purposes the density of liquids is obtained by means of hydrometers, which are graduated on the stem to give direct density readings. Such methods are far too inexact for physico-chemical purposes.

The density of a liquid is most easily and accurately obtained by means of a specific gravity bottle or a pyknometer. The Perkin form of the pyknometer is perhaps the easiest to manipulate; this consists of a glass bulb A (Fig. 20) fitted with two tubes *a* and *b* of medium-walled capillary tube of about 1·5 mm. bore, the one *a* being drawn out to a point and the other slightly constricted at *d*; above *d* a small bulb *e* is blown. A ring is etched round the tube at *d* to fix the capacity. There is, then, between the point of the pipette and the constriction at *d*, a definite volume, which may be determined. The ends of *a* and *b* are provided with two small glass caps *f*, which should always be put on when the pipette is being weighed or is standing in the balance case. The pyknometer is cleaned by washing with a bichromate and sulphuric acid mixture, and then distilled water. To dry it, alcohol is drawn through, and finally re-distilled ether. The last traces of ether are removed by blowing air through it from a bellows. Pyknometers should never be heated to dry them, for this occasions slight volume changes which do not at once disappear when the vessel is cooled.

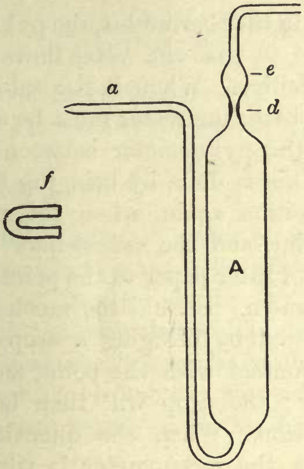

Fig. 20.

To make a determination, the pyknometer is first weighed empty; this is best accomplished by hanging it to the balance beam by a loop of platinum wire. It is then filled with freshly-boiled distilled water by dipping the point under the water and sucking gently at a piece of rubber tubing attached to the other end. When filled, it is allowed to stand in a thermostat for about twenty minutes, so that the temperature of the water may be known.

When placed in the thermostat, the pyknometer should be slightly tilted, so that the water flows away from the point into the bulb *e*. When it has taken on the temperature of the bath, the water must be adjusted so that it exactly fills the pyknometer between the point and the mark *d*. This is done by bringing the pyknometer to the level position again, when the water will flow back to the point, and the excess may be removed by holding a piece of filter paper to the point until sufficient has been withdrawn. Should too much be withdrawn, it may be replaced by bringing a drop of water on a glass rod into contact with the point, and again tilting the pyknometer; the drop will then be drawn in by capillary attraction. When the quantity of water is exactly adjusted, the pyknometer is tilted so that the water leaves the point and enters the bulb; this prevents loss of liquid during drying. The vessel is then carefully dried, the caps are placed on *a* and *b*, and it is put in the balance case. Since the pyknometer will not stand by itself, it is usual to stand it in a narrow beaker. After half an hour has elapsed it is weighed. Several determinations of the weight of water contained in the pyknometer should be made, and the mean weight used in subsequent calculations. The water is now removed, and the pyknometer dried, and filled with the liquid whose density is to be determined, and the process repeated.

If W be the weight of water and W′ the weight of the second liquid held by the pyknometer, then the relative density of the liquid compared with water is given by

$$d^t_t = \frac{W'}{W},$$

or, compared with water at 4°,

$$d^t_{4^\circ} = \frac{W'}{W} \cdot d_t,$$

where d_t is the density of water at t°. For absolute determinations this must be reduced to vacuum standard.

$$d^t_{4^\circ} = \frac{W'}{W} \cdot d_t - \left(\frac{0{\cdot}0012(W'_1 - W)}{W}\right).$$

A table of the density of water at various temperatures will be found in the Appendix (Table II.).

Determination of Density at the Boiling Point. The determination of the densities of liquids can be carried out at all temperatures below the boiling point, by the method described above, but the method requires slight modification if the density is to be determined at the boiling point.

The method is due to Ramsay and Lothar Meyer. The pyknometer consists of a thin-walled glass bulb A (Fig. 21) of about 2·5 c.c. capacity, which is fitted with a single capillary tube B, bent as in the diagram. The pyknometer is filled with liquid in the following way: a stout-walled tube C (Fig. 21), fitted with a side tube D and a rubber stopper E, is half filled with liquid, and the pyknometer, supported by a wire F, is placed so that it just dips below the surface. The tube D is then attached to a water pump and partially exhausted. On allowing air to re-enter the apparatus, by opening the tap G, some of the liquid runs into the pyknometer.

The process is repeated several times until the bulb is almost full. This method of filling is adopted in cleaning the pipette, and in the determination of its volume.

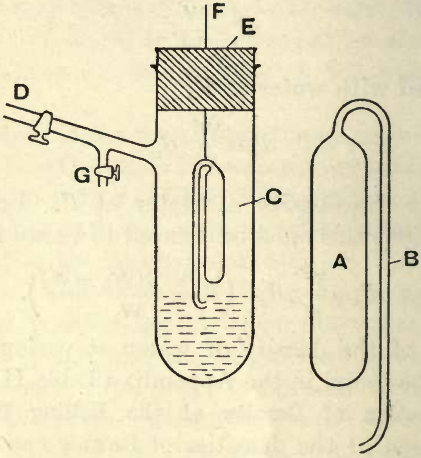

FIG. 21.

Having almost filled the pyknometer with the liquid whose density is to be determined, it is suspended by a platinum wire in a wide-necked bulb A (Fig. 22), so that it is just above the liquid in the bulb. The bulb contains the same liquid as the pyknometer. The tube is fitted with a side tube B, to which a condenser C is attached. A thermometer *t*, supported by a rubber stopper, is placed with its bulb on a level with the pyknometer bulb. The liquid in the bulb is then raised to the boiling point and kept there until the pyknometer and its contents have attained the temperature of the boiling liquid. The heating causes the liquid in the pyknometer to expand and gradually fill the whole vessel, the excess being expelled from the tip. When the pyknometer has acquired the temperature of the bath, *i.e.* when no more liquid is expelled from the tip, it is withdrawn and cooled quickly, so that the liquid in the capillary is withdrawn into the bulb, leaving behind any drop which may be hanging on to the point. The pyknometer is placed in a beaker and allowed to stand in the balance case for half an hour, after which it is weighed.

Since the volume of the pyknometer changes with temperature, we require to know the coefficient of cubical expansion of glass, before the density can be calculated from the measurements. To determine this, the weight of the pyknometer filled with air, and with water at two different temperatures is required.

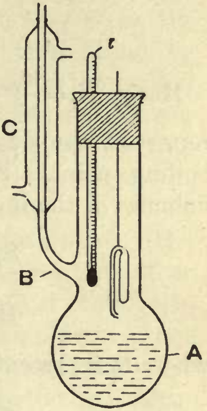

FIG. 22.

If w_1 and w_2 represent the weights of water contained by the pyknometer at $t_1°$ and $t_2°$, d_1 and d_2 the density of water at the two temperatures respectively, and v_1 and v_2 the corresponding volumes, then

$$v_1 = \frac{w_1}{d_1} \quad \text{and} \quad v_2 = \frac{w_2}{d_2}.$$

The difference in the volume of the pipette at the two temperatures is given by

$$3a(t_2 - t_1) = v_2 - v_1,$$

where a is the coefficient of cubical expansion of glass.

Since $$v_2 - v_1 = \frac{w_2}{d_2} - \frac{w_1}{d_1},$$

we have $$3a = \frac{\dfrac{w_2}{d_2} - \dfrac{w_1}{d_1}}{t_2 - t_1}.$$

If T represents the boiling point of the liquid whose density is being determined, then the volume of the pyknometer at the boiling point is

$$v_{\mathrm{T}} = v_1 + 3a(\mathrm{T} - t_1)$$
$$= \frac{w_1}{d_1} + 3a(\mathrm{T} - t_1).$$

Hence $d_{\mathrm{T}} = \frac{w_{\mathrm{T}}}{v_{\mathrm{T}}}$ can be determined where d_{T} and w_{T} represent the density and weight of the liquid at the boiling point. From d_{T}, the molecular and specific volumes of the liquid can be readily calculated.

$$\text{Specific Volume} = \frac{1}{d_{\mathrm{T}}},$$

$$\text{Molecular Volume} = \frac{\mathrm{M}}{d_{\mathrm{T}}},$$

where M represents the molecular weight.

The determination of the density of a liquid at the boiling point is more easily carried out, if a pyknometer devised by Crompton is used instead of the Ramsay form. This instrument consists of a bulb A (Fig. 23), of about 5 c.c. capacity, fitted with two side tubes *a* and *b*. The one *a* is drawn out to a small hook-like point, and the other *b*, somewhat longer than the side tubes of ordinary pyknometers, is constricted near the bulb and bent at the top, as indicated in the diagram. A mark *c* is etched round the glass at the constriction. It will be at once obvious that this pyknometer is much more easily cleaned, emptied and filled, than the Ramsay form. The volume

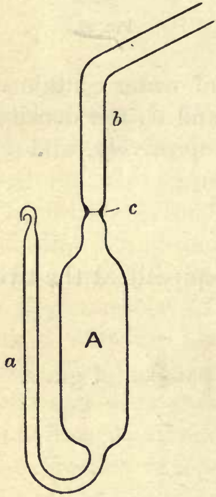

FIG. 23.

of the pyknometer is determined in exactly the same way as already described. To determine the density of a liquid at the boiling point, the pyknometer is filled with the cold liquid by immersing it in the liquid until the point is covered, and then filling by gently drawing at *b*. Then it is immersed in the boiling substance, and kept there until the temperature is constant. When this is the case the liquid is drawn into the pyknometer, so that it stands slightly above the mark *c*. A piece of rubber tubing closed at one end by a short glass rod is then slipped on to the tube *b*. The liquid may now be brought exactly to the mark *d*, either by pushing the rod further into the tubing, if the pipette is too full, or drawing it out a little, if the pipette is not full enough. The vessel is then withdrawn from the bath, cooled, dried and weighed. The method of calculation is exactly the same as that previously described. It is obvious that such a pyknometer may be used advantageously for determinations at all temperatures.

Determination of the Density of Liquids of high Freezing Point. A method for determining the density of liquids which solidify between atmospheric temperature and 150°, has been devised by Crompton. It involves the use of a pyknometer shaped somewhat like a pipette (Fig. 24). The bulb A is drawn out at its lower end to a short capillary point, the upper tube *b* is a capillary, and has a mark *d* etched on it. The volume of the pipette is determined by the ordinary method of weighing it empty and full of water at a known temperature.

To determine the density of a liquid of high freezing point, a quantity of the solid substance is placed in a tube B (Fig. 24), which is surrounded by a slightly larger tube C. This serves as an air jacket to the inner tube. These tubes are then placed in a bath at a temperature higher than the melting point of the solid substance. When the solid has melted, a small stirrer *s*, of platinum wire, and a thermometer *t* are inserted into the molten substance. The pyknometer is then placed in the tube B, and when its temperature has become that of the surrounding bath, the liquid is drawn into it until the mark *d* is reached. A piece of rubber tube, closed at one end by a glass rod, is then slipped over the end of *b*, and the bath and contents kept at constant temperature for 10 minutes; the liquid in the pyknometer is then brought exactly to the mark by means of the rod in the rubber tubing. Then the pipette is withdrawn from the bath, and the liquid at once solidifies. The tube is cleaned and weighed, and the density calculated. An alternative method of using this pipette consists in having two marks on the stem, *a* and *d*, one at either end of the capillary. The volume of the pyknometer is known when filled to either mark; this is ascertained in the usual way, by filling with water to one mark and weighing, and then filling to the other mark and re-weighing. In this way the capillary is calibrated, and the volume at any point in it can be obtained by calculation. In filling with the liquid whose density is to be determined, the level may therefore be brought to *any* point between *a* and *d*, and no exact

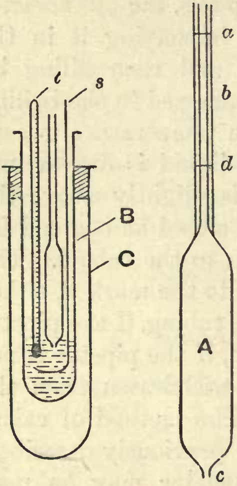

FIG. 24.

adjustment, which is often a matter of considerable difficulty, is necessary.

EXPERIMENTS

(i) *Determine the value of* D_4^{25} *for Absolute Alcohol.* Carefully clean and dry a pyknometer. Weigh it empty, filled with water at 25°, and with alcohol at the same temperature. From the weights obtained calculate D_4^{25}, using the density of water at 25° given in Table II. Appendix, and the formula

$$D_4^{25} = \frac{W_l}{W} d_{25} - \left(\frac{0{\cdot}0012(W_l - W)}{W}\right)$$

where W_l is the weight of the alcohol, W the weight of water, and d_{25} the density of water at 25°.

(ii) *Determine the Molecular Volume of Benzene at its Boiling Point.* Take a small pyknometer of the shape and size recommended in the general description. Clean, dry and weigh it. Then fill it with water at ordinary temperature, which must be noted, and weigh again. Then hang it in a steam bath until it has acquired the temperature of the steam; cool, dry and re-weigh. The barometric height must now be read, and the boiling point of the water obtained from Table III. Appendix. Empty the pyknometer and dry it, then fill it with benzene and heat to the boiling point; cool and weigh again. From the data thus obtained, calculate the molecular volume by the method described above.

Having determined the molecular volume for benzene, repeat the process, using chlorbenzene, brombenzene, iodobenzene, nitrobenzene and aniline, and in this way obtain the effect which is produced on the molecular volume when hydrogen is substituted by the various groups.

It is unnecessary to weigh the pyknometer filled with water in any but the first determination: the values found from this serve in every other case.

These experiments may be carried out with either the Ramsay or the Crompton pyknometer, the latter is, however, much easier to manipulate.

(iii) *Determine the Density of Azobenzene at* 70°. Place about 25 grams of re-crystallised *azobenzene* in a test tube, and melt it in a bath of water (see Fig. 24). Then fill a Crompton pipette, whose volume you have previously determined. When the temperature is definite, and the pyknometer exactly filled, withdraw the pipette, cool, clean and weigh it.

3. Density of Gases

The density of a gas is determined by directly weighing the gas in a strong glass bulb of about 200 c.c. capacity (Fig. 25). The bulb is attached to a stout-walled capillary tube which is provided with a well-fitting tap. This must be carefully greased before use. The volume of the bulb must be determined first of all: this is done by weighing it filled with air and then with water at a known temperature. To fill such a globe with water, it must be exhausted, and the tap opened when the tube is dipping under water which has been previously boiled. It is then placed in a thermostat until it has taken on the temperature of the bath. Then it is dried and weighed to the nearest centigram. The volume can now be calculated as described in Chapter II.

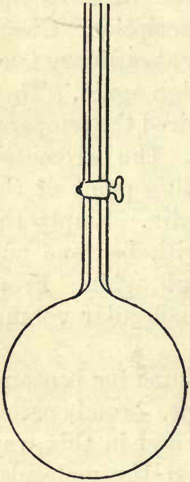

Fig. 25.

Errors due to buoyancy of the air may be eliminated by counterpoising the globe by one of equal volume.

The globe is then emptied and washed out successively with alcohol and ether, and finally exhausted to remove the last traces of ether. It is then filled with the gas whose density is to be determined, the temperature and barometric pressure are noted, and the bulb weighed. For the method of filling a bulb with a gas see Chapter IV.

If W be the weight of the exhausted globe, W' the weight of the globe filled with gas, and V_0 the corrected volume, then the absolute density, or the weight of 1 c c., is given by

$$d = \frac{W' - W}{V_0}.$$

The volume V_0 is obtained from the experimentally determined volume by the expression

$$V_0 = \frac{V . 273 . P}{(273 + t)760},$$

where P and t are the pressure and temperature under which the bulb was filled.

Since the gram molecular weight of a gas at 0° and 760 mm. occupies 22400 c.c., it follows that the molecular weight of a gas can be obtained directly from the value of d.

$$M = 22400d.$$

One generally determines the density of a gas by comparison with air, and when this is done, it is unnecessary to determine the volume of the globe.

If W is the weight of the vacuous globe, W' that of the globe filled with air, and W'' filled with the gas in question, then

$$d = \frac{\text{Wt. of the gas}}{\text{Wt. of air}} = \frac{W'' - W}{W' - W},$$

if air be taken as the unit. If hydrogen be taken as the unit, the expression then becomes

$$d=\frac{W''-W}{W'-W}\cdot d_1.$$

where d_1 is the density of air at normal temperature and pressure.

Experiment

Determine the Density of Carbon dioxide at Ordinary Temperature. Determine the weight of a vacuous globe, then fill it with dry air, noting the temperature and pressure under which it is filled. Weigh it full of air, and then fill it with dry carbon dioxide and again weigh. The density of carbon dioxide at the given temperature is obtained by the expression

$$d=\frac{\text{Weight of Carbon dioxide}}{\text{Weight of air}}\times d_1,$$

where d_1 is the density of air under the conditions of the experiment.

If the density of air at 0° and 760 mm. be taken as unity, then

$$d_1=1\times\frac{P}{760}\times\frac{273}{273+t}.$$

Since all gases are similarly affected by temperature and pressure, the expression

$$d=\frac{\text{Weight of Carbon dioxide}}{\text{Weight of air}}$$

gives the density of carbon dioxide at 0° and 760 mm., so that, assuming air has a density of 14·4 when compared with $H=1$, the molecular weight of carbon dioxide will be obtained from the expression

$$M=d\times 14{\cdot}4\times 2,$$

since the molecular weight is twice the density.

4. Determination of Vapour Density

Many substances, both solid and liquid, vaporise easily. It is customary, in settling questions of molecular weight, to determine the density of their vapours at temperatures above the boiling point. The density determinations described here are not, and do not need to be, exact, for the sole point of the determination is to arrive at the molecular weight, and an error of five per cent. in the density will not influence the decision with regard to molecular weight. In some cases, however, abnormal vapour densities are obtained, which are either larger or smaller than is required to be in accord with other known facts. These abnormalities are explained, in the case of vapour densities which are too small, by the assumption that the molecule has split up into smaller molecules, *i.e.* it has dissociated. In the other case, where the vapour density is too large, it is assumed that two or more molecules have combined together, *i.e.* an association has taken place. There are several methods for the determination of vapour density for the purpose of settling the molecular weight, the most important of which, in the order of their accuracy, are: (i) Dumas' Method, (ii) Hofmann's Method, (iii) Victor Meyer's Method.

(i) **Dumas' Method** consists in weighing a known, or easily determined volume of a vapour. The experiment is carried out in a glass bulb A (Fig. 26) of from 30–250 c.c. capacity, fitted with a tube B which is drawn out to a fine point.

The globe is weighed, and then 2–3 grams of the substance whose vapour density is to be determined are introduced. This is done by warming the globe and then dipping the capillary end into the liquid or molten solid. As the bulb cools, some of the substance will be drawn in. The globe is then placed in a bath so that only about 2–3 cm. of the side tube project, and it is heated to a temperature about 20°–30° above the boiling point of the substance it contains. The heating is continued until no more vapour is expelled from the point, and then the temperature of the bath and the atmospheric pressure are taken, and the end of the tube is carefully sealed with a blowpipe.

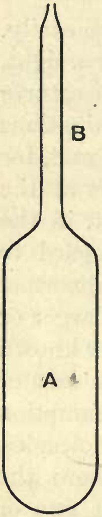

Fig. 26.

The bulb is removed from the bath, cooled, cleaned, dried and weighed. The end is then broken off under boiled water, and the bulb filled with water and again weighed, care being taken to collect any splinters of glass which may be broken off, and to weigh them along with the bulb full of water. A bubble of air is often left when water is let into the bulb, this is due to air which has not been expelled by the vapour and must be allowed for.

If w is the weight of the bulb filled with air at the temperature t and pressure p, w' the weight of the bulb filled with the substance, t' the temperature and p' the pressure under which it was sealed, and w'' the weight of the bulb filled with water, then

$$w''-w$$

gives the weight of water required to fill the bulb. If the density of water at the temperature at which it was weighed is given by d, then

$$V=\frac{w''-w}{d},$$

where V is the volume of the flask.

The weight of the vapour W is now given by the expression

$$\mathsf{W}=w'-w+\mathsf{V}\left(0{\cdot}001293\,.\,\frac{p}{760}\,.\,\frac{273}{273+t}\right).$$

The weight of an equal volume of air W' at t' and p' is given by

$$\mathsf{W}'=\mathsf{V}\left(0{\cdot}001293\,.\,\frac{p'}{760}\,.\,\frac{273}{273+t'}\right).$$

$$\text{The vapour density}=\frac{\mathsf{W}}{\mathsf{W}'}$$

when 0·001293 represents the weight of 1 c.c. of air at 0° and 760 mm.

In determining the vapour density of substances which have a low vapour pressure at ordinary temperatures, and, in general, any liquid boiling above 100°, Crompton has shown that it is quite unnecessary, in molecular weight determinations, to seal the bulb. His method of procedure is exactly the same as that described above up to the point where the bulb is sealed. In this method, when the substance is all vaporised and no more vapour is emitted from the tube, the bulb is withdrawn from the bath and quickly cooled and then weighed. The volume of the apparatus is obtained either by filling it with water and weighing, or by using a thin walled vessel immersing it in water and measuring the increase in the apparent volume of the water. The calculation of the vapour density by this method is also much simpler.

If w is the weight of the bulb filled with air, and w' filled with air and the small amount of the substance whose vapour originally filled the bulb, then $w'-w$ gives the weight of the substance, and no correction is necessary for buoyancy of the air.

If V is the volume of the bulb, then

$$\mathsf{W}=\mathsf{V}\left(0{\cdot}001293\,.\,\frac{\mathsf{P}}{760}\,.\,\frac{273}{273+t}\right)$$

gives the weight of the same volume of air under the experimental temperature and pressure t and P. The density then

$$=\frac{w'-w}{\mathsf{W}},$$

where W is the weight of the air under the experimental conditions.

EXPERIMENTS

(i) *Determine the Vapour Density and Molecular Weight of Acetone.* Proceed exactly as described above. Introduce about 2–3 c.c. of re-distilled acetone into the bulb and heat in a boiling water bath. Test for the emergence of vapour at the point by holding a cold metal surface close to the point; if vapour is being expelled it will condense on the metal and can be seen. Calculate the density to the standard H=1, air being taken as 14·4.

(ii) *Determine the Vapour Density of Brombenzene.* In this experiment use an oil bath at about 180°. When the vapour is no longer driven from the tube, remove the bulb and cool as quickly as possible. Clean the bulb by rubbing it with a duster moistened with chloroform, then dry it and weigh. Calculate the result by the second method given above.

(ii) **Hofmann's Method** determines the volume of a given weight of vapour. The determination is carried out in a fairly stout-walled tube A (Fig. 27) about 100–120 cm. long and 2 cm. diameter. The tube is graduated in millimetres, and the relative volume of the millimetre divisions is also known. The tube is filled with dry mercury and stood in a mercury trough B; it is surrounded by a glass jacket C which is fitted with two side tubes D and E. The substance, whose vapour density is to be determined, is contained in a small stoppered tube F; this is carefully weighed and placed into the bottom of the tube A, when it quickly rises to the top of the mercury. The vapour of a liquid boiling a few degrees above the boiling point of the substance in the tube is admitted by the side tube D, the condensed vapour running out at E. This heats up the tube and vaporises the substance in F, and the mercury is depressed. When the vapour of the heating liquid is no longer condensed, *i.e.* after about twenty minutes, the volume of the vapour in the tube A is noted, and the height of the column of mercury *hl* is measured.

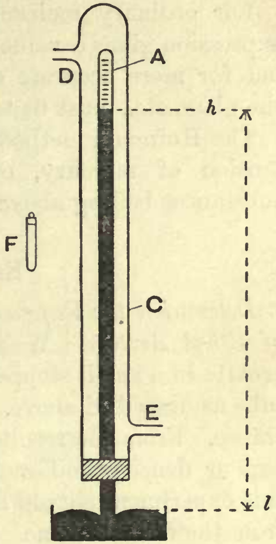

FIG. 27.

If W is the weight of the substance, V the volume, t the temperature of the heating jacket, *i.e.* the boiling point of the liquid used, P the barometric pressure, h the height of the mercury column, and m the vapour pressure of mercury at the temperature of the experiment (see Table IV. Appendix), then the weight of a volume V of air at 0° and 760 mm. is given by

$$\frac{V(P-h-m)}{760} \cdot \frac{273}{273+t} \cdot 0{\cdot}001293 = W'.$$

Hence $$\text{Density} = \frac{w}{w'}.$$

For ordinary molecular weight determinations, this expression gives a value which is quite accurate enough, but for more accurate determinations, the expansion of the glass, etc., must be taken into account.

The Hofmann method, owing to the increasing vapour tension of mercury, ought not to be employed for substances boiling above 250°.

EXPERIMENT

Determine the Vapour Density and Molecular Weight of Ethyl Acetate. Weigh out about 0·1 gram of ethyl acetate in a small stoppered tube, insert it in a Hofmann tube as described above. Use steam as the heating substance. From the results of the experiment calculate the vapour density and molecular weight. The results of this experiment should not differ more than ±2 per cent. from the correct value.

(iii) **Victor Meyer's Method** determines the volume of air displaced by a given weight of a substance in the state of vapour, and, since the volume of air displaced would occupy the same volume as the vapour of the substance if it were raised to the same temperature, Victor Meyer's method gives, indirectly, the volume occupied by the vapour.

The determination is usually carried out in a vessel consisting of a bulb A (Fig. 28) of about 150 c.c. capacity, connected to a long tube B of about 7 mm. diameter. This tube is widened out at the top, and has a side tube C attached to it, and is closed by a rubber stopper S. The bulb is placed in a glass or metal jacket D, which contains about 50 c.c. of a liquid that can be used to give a temperature about 30° higher than the boiling point of the substance under investigation. A small

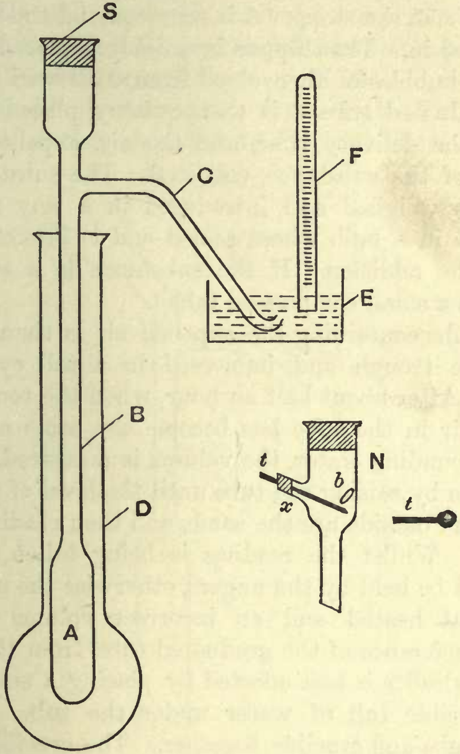

FIG. 28.

plug of asbestos is placed at the bottom of **A**, to save it from fracture when the substance is dropped in. The side tube **C** dips under water contained in a glass dish **E**, and the expelled air is received in a graduated eudiometer tube **F**.

To carry out a determination, the liquid in **D** is raised to the boiling point and kept there throughout the experiment. When the temperature of the apparatus is constant, *i.e.* when no more bubbles of air are driven out of the tube C, the stopper S is removed and the substance is dropped in. The stopper is quickly replaced, and the first two bubbles of air evolved from C allowed to escape. The graduated tube F is then quickly placed over the end of the delivery tube, and the air, expelled by the vapour of the substance, collected. The substance, if a liquid, is weighed and introduced in a tiny stoppered bottle, or in a bulb whose sealed end is broken off just before the addition. If the substance is a solid it is added as a small compressed tablet.

The tube containing the expelled air is then removed from the trough and immersed in a tall cylinder of water. After about half an hour, when the temperature of the air in the tube has become the same as that of the surrounding water, the volume is measured. This is best done by raising the tube until the level of the water inside and outside are the same, and then reading off the volume. Whilst the reading is being taken, the tube must not be held by the fingers, otherwise the air will be somewhat heated and an incorrect volume obtained. The transference of the graduated tube from the trough to the cylinder is best effected by placing a small porcelain crucible full of water under the tube, and then lifting tube and crucible together. The crucible is then sunk under the water of the cylinder, with the tube still held in it, until the bottom of the tube is under the level of the water in the cylinder, and then the crucible is allowed to fall to the bottom.

There are many devices which render it unnecessary to remove the stopper when the substance is introduced; one of these is illustrated in N (Fig. 28). N is the neck of the ordinary apparatus, fitted with a small side tube *x*, this is closed by a rubber stopper through which a glass rod, flattened at one end, is introduced. The substance rests on this flattened rod until the temperature is constant, and then it is allowed to fall into the apparatus by twisting the rod through an angle of 90°.

An exceedingly convenient form of the Victor Meyer apparatus is that depicted in Fig 29. It consists, as will be seen, of three parts, which are carefully ground into one another. The top part c also obviates the necessity of a stopper, and when in position *a*, holds the substance until the temperature is constant, and when twisted into position *b*, drops it into the bulb. This form of apparatus is very easily cleaned and dried, and, as

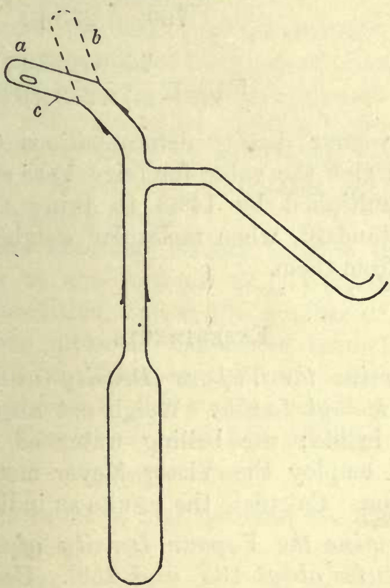

Fig. 29.

the parts can be made to standard size, the breaking of one piece does not mean a new apparatus, as is generally the case with the other form.

If V is the volume of air measured at a temperature t and barometric pressure P, and m the tension of aqueous vapour at $t°$ (see Table V. Appendix), then

$$\text{The vapour density} = \frac{\mathsf{W}}{\frac{\mathsf{V}(\mathsf{P}-m)}{760} \cdot \frac{273}{273+t} \times 0{\cdot}001293}$$

$$= \frac{760\,\mathsf{W}(273+t)}{\mathsf{V}(\mathsf{P}-m) \times 273 \times 0{\cdot}001293}.$$

All the vapour density determinations described in this section give the value for (air = 1) as standard, and must be multiplied by 14·33 to bring them to the hydrogen standard, when molecular weights are to be calculated from them.

EXPERIMENTS

(i) *Determine the Vapour Density and Molecular Weight of Methyl Iodide.* Weigh out about 0·3 gram of methyl iodide; use boiling water as the heating liquid, and employ the Victor Meyer method for the determination. Calculate the results as indicated above.

(ii) *Determine the Vapour Density of Acetic Acid at temperatures about* 135° *and* 250°. Use the Victor Meyer method, and weigh out about 0·1 gram for each experiment. For the lower temperature use a solution of 120 grams of anhydrous calcium chloride in 100 of water at its boiling point as the heating liquid, (in this case the bulb must be entirely immersed in the heating liquid,) and for the higher temperature use boiling quinoline.

Calculate the vapour density and molecular weight in each case. If M represents the molecular weight at the lower temperature, M' at the higher temperature, and m the molecular weight corresponding to the formula $C_2H_4O_2$, then the association factor k may be calculated by the expressions

$$\frac{\mathsf{M}}{m}=k, \text{ and } \frac{\mathsf{M}'}{m}=k'.$$

(iii) *Determine the Degree of Dissociation of Chloral Hydrate.* Weigh out about 0·2 gram of chloral hydrate in a small stoppered tube; determine the vapour density at about 108°, using a solution of 40 anhydrous calcium chloride in 100 of water at its boiling point as the heating liquid. Repeat the experiment at 184°, using aniline as the heating liquid.

If D be the observed density, and d the density corresponding to the formula $CCl_3.CH(OH)_2$, a the degree of dissociation, and n the number of molecules into which one molecule dissociates, then 1 molecule becomes $1-a+na$. That is, the ratio of the number of molecules present to the number which would have been present if no dissociation had taken place is

$$1+a(n-1):1.$$

This ratio is equal to that between the observed and calculated densities.

$$\frac{1}{1+(n-1)a}=\frac{\mathsf{D}}{d} \text{ or } a=\frac{d-\mathsf{D}}{(n-1)\mathsf{D}}.$$

(iv) *Determine the Degree of Dissociation of Ammonium Chloride at* 350°. For this experiment the apparatus should be made of Jena glass or quartz. Weigh out about 0·1 gram of ammonium chloride and compress it into a tablet. The heating may be effected by a bath of molten tin, with careful regulation of temperature. The electrical method of heating can also be employed in this case. For this, the bulb of the apparatus is covered with a thin piece of asbestos paper, around which a long length of thin platinum wire is wound. The ends of the wire are connected through a fairly large adjustable resistance with the electric main. The bulb is then placed in a metal box and packed round with asbestos. By varying the resistance, the temperature can be brought to about 350°. The experiment is then carried out in the usual manner. Calculate the degree of dissociation from your results.

CHAPTER VI

ATOMICITY

KNOWLEDGE of the density of a gaseous element is not sufficient to fix its atomic weight. Before this value can be known, it is necessary to determine its atomicity, *i.e.* the number of atoms contained in a molecule. Generally, the atomicity is arrived at by a consideration of the volume relationships with which the given gaseous element enters into combination with other elements, or in those cases where both atomic weight and molecular weight are known, by simply dividing the former by the latter. The term "atomicity" must not be confused with "valency," as it is so often done in text-books. Occasionally it happens that neither of these methods is available, *e.g.* in the case of argon and its congeners, and in such cases, information must be sought from the physical properties, notably the ratio of the specific heats. The specific heat of a gas may be measured either at Constant Volume c_v or at Constant Pressure c_p. If a gas be heated, and its volume kept constant, the heat added is used entirely in increasing its kinetic energy and in doing intramolecular work. On the other hand, if a gas be heated and its volume allowed to change so that the pressure remains constant, the added heat is used in increasing the kinetic energy, in performing intramolecular work, and in doing external work in the process of increasing the volume of the gas.

The molecular heat of a gas at constant volume is the quantity of heat required to raise the temperature of the molecular weight, in grams, through one degree, the volume being kept constant. If in heating a molecular quantity of a gas through one degree at constant volume, it is assumed that all the heat goes to raise the temperature of the gas, *i.e.* to increase its kinetic energy, the molecular heat will be equal to 3 calories.

The molecular heat of a gas at constant pressure is the quantity of heat required to raise the temperature of the molecular weight through one degree, the volume being allowed to increase and the pressure being kept constant. If in this case it be again assumed that no intramolecular work is done, the molecular heat at constant pressure will be equal to 5 calories, of which 3 calories are used in increasing the kinetic energy of the gas, and 2 calories are used in doing external work.

The above assumption is only true for monatomic gases, for here, since there is only one atom in the molecule, no intramolecular work is possible. Hence for monatomic gases, the ratio of the specific heats is given by the expression

$$\frac{C_p}{C_v}=\frac{5}{3}.$$

If the gas is polyatomic, and x represents the heat used up in doing intramolecular work, the ratio of the specific heats is given by the expression

$$\frac{C_p}{C_v}=\frac{5+x}{3+x}.$$

The value of x depends on the number of atoms in the molecule, and generally increases with the number of atoms.

Hence it follows that the larger the number of atoms in the molecule, the smaller will be the ratio of the specific heats. For diatomatic gases the value is about 1·40.

From a chemical point of view the ratio $\frac{C_p}{C_v}$ is extremely important, and as the separate determination of the two factors of the ratio is a tedious and difficult operation, it is better for the present purpose to determine the ratio directly.

There are two methods for determining the ratio of the specific heats, due to Clement and Desormes, and Kundt respectively.

(i) **Clement and Desormes' Method.** The apparatus necessary for the determination by this method consists of a large flask A (Fig. 30), fitted with a wide neck B,

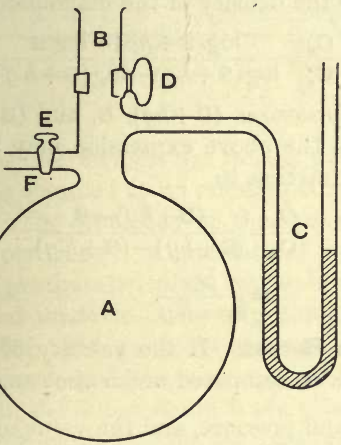

Fig. 30.

which is closed by a stopcock D. This has an aperture which is nearly as wide as the neck of the flask. Two side tubes are fitted on to the neck of the flask, the one C, bent in the form shown in the diagram constituting a manometer, and the other F having a stopcock E.

To determine the ratio of the specific heats, the flask is filled with the gas at a pressure slightly above atmospheric. The pressure is noted by means of the manometer, and the large stopcock opened to the air for a moment, so that the pressure of the gas may sink adiabatically to that of the air. The tap is then closed, and the flask allowed to stand for a few minutes until its contents, which have been cooled by the adiabatic expansion, have been raised to the atmospheric temperature again. The pressure is then noted.

If B is the barometric pressure in mm. of water, h the difference of level of the liquid in the manometer in millimetres before opening the tap, and h' after opening the tap, and g the density of the manometer liquid; then

$$\frac{C_p}{C_v}=\frac{\log(B+hg)-\log B}{\log(B+hg)-\log(B+h'g)}.$$

Since the pressures $(B+hg)$, B, and $(B+h'g)$ are not very different, the above expression may be changed, as a first approximation, to

$$\frac{C_p}{C_v}=\frac{(B+hg)-B}{(B+hg)-(B+h'g)}$$
$$=\frac{hg}{hg-h'g}.$$

(ii) **Kundt's Method.** If the velocity of sound in two different gases be compared under the same conditions of temperature and pressure, and the value of $\frac{C_p}{C_v}$ for one of them is known, then the value of the ratio for the other gas can be calculated.

If V_1 be the velocity of sound in a gas A, and V_2 that in a gas B, then if d_1 and d_2 be their respective densities, and p the pressure under which the velocities were determined, it follows that:

$$V_1 = \sqrt{\gamma_1 \frac{p}{d_1}} \quad \text{and} \quad V_2 = \sqrt{\gamma_2 \frac{p}{d_2}},$$

where γ_1 and γ_2 respectively represent the ratio of the specific heats.

Dividing these two expressions, the following relationship is obtained:

$$\frac{V_1}{V_2} = \sqrt{\frac{\gamma_1 d_2}{\gamma_2 d_1}} \quad \text{or} \quad \gamma_1 = \gamma_2 \cdot \frac{d_1}{d_2} \cdot \left(\frac{V_1}{V_2}\right)^2.$$

To determine the ratio of the specific heats by this method, a wide glass tube about 1½ metres long is employed (Fig. 31). This is fitted with two side tubes A and B. Into one end of the tube a glass rod CD is placed, which is clamped at its middle point by a tightly fitting cork E. The other end of the tube is closed by a tightly fitting plunger F. A quantity of a light powder, lycopodium or precipitated silica, is placed on the bottom of the tube, and made to lie evenly along the tube by tapping the sides. The gas to be measured is introduced by the side tube A, and the air expelled by B. When the tube is full, the tubes A and B are closed by rubber caps, and a damp cloth is then drawn along the rod CD, so that it vibrates longitudinally and emits a note. The vibrations are communicated to the gas in the tube, and cause the powder to arrange itself into a series of small

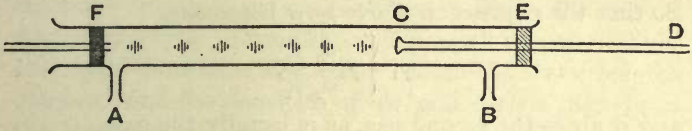

FIG. 31.

heaps, representing the nodes of the vibration. Should the nodes not be well defined, the plunger F is moved backwards or forwards until they are. The distance between two heaps is then measured. If l_1 be the distance between two nodes, *i.e.* two heaps, then $2l_1$ is the wave length of the note emitted by the rod, and $\mathsf{V}_1 = 2l_1 n$ gives the velocity of sound, where n is the vibration number of the note.

A second gas is then introduced, one whose ratio is known, and the value l_2 obtained for the distance between the nodes. Then $\mathsf{V}_2 = 2l_2 n$.

Hence it follows that the velocities are in the same ratio as the distances between the nodes.

$$\frac{\mathsf{V}_1}{\mathsf{V}_2} = \frac{l_1}{l_2}.$$

So that the expression above now becomes

$$\gamma_1 = \gamma_2 \frac{d_1}{d_2} \cdot \frac{l_1^2}{l_2^2},$$

and if air is the second gas, as is usually the case,

$$\gamma_1 = 1{\cdot}405 \frac{d_1}{d_2} \cdot \frac{l_1^2}{l_2^2}.$$

EXPERIMENTS

(i) *Determine the Ratio of the Specific Heats, and the Atomicity of Oxygen.* Use the Clement and Desormes' method for this experiment. Place α-bromnaphthalene in the manometer tube; this has a density 1·481 at 25°. Now open the stopcock D, and lead in dry oxygen by placing the delivery tube well into the flask. When all the air has been expelled, and the flask is full of oxygen, withdraw the delivery tube and close D. Then attach the oxygen supply to the side tube F, open the stopcock E and allow more oxygen to enter, until the levels of the manometer liquid are about 12 cm. apart. Close E and allow the flask to stand for 15 minutes in some place free from draughts, and of fairly constant temperature. Read off the difference in height of the two sides of the manometer liquid, and open the tap D for about two seconds; the liquid will then be at the same height in both arms of the manometer. Allow the flask and contents to warm up to the atmospheric temperature, (this takes about ten minutes,) and then read the levels of the liquid in the manometer again. From the pressures obtained, calculate the ratio of the specific heats, and deduce the atomicity of oxygen.

(ii) *Determine the Ratio of the Specific Heats of Carbon Dioxide.* Fit up the Kundt apparatus, and determine the wave length of the note emitted in air, by the method described above. Then fill the tube with carbon dioxide, and again determine the value. From the wave lengths obtained, and the densities of air and carbon dioxide at the temperature and pressure of the experiment, calculate the value $\frac{C_p}{C_v}$ for carbon dioxide, being given that the value for air is 1·405.

CHAPTER VII

DETERMINATION OF MOLECULAR WEIGHTS IN SOLUTION

VAN'T HOFF has shown that a substance in dilute solution is in a similar condition to that of a gas, and that it obeys laws similar to those applying to gases. It has already been shown (Chapter IV.) that a knowledge of the weight, volume, temperature and pressure of a gas enables one to calculate its molecular weight. In the same way, substituting for pressure the osmotic pressure, it is possible, using the same four quantities, to calculate the molecular weight of a dissolved substance.

The gram molecular weight of a gas is that weight of a gas measured at 0° and 760 mm. pressure, which has a volume of 22·40 litres. In the same way the gram molecular weight of a dissolved substance is that weight which, when dissolved in 22·40 litres of solution at 0°, has an osmotic pressure of 760 mm.

This fact being allowed, it follows that the direct measurement of the osmotic pressure of a solution of known concentration may be used to determine the molecular weight of the dissolved substance. When a substance is dissolved in a solvent, the vapour pressure of the solvent is decreased, the boiling point is raised, and the freezing point is lowered. These three changes have been shown by van't Hoff to be closely connected with the osmotic pressure, and are made use of to determine the molecular weight of substances in solution. These determinations may be regarded as indirect measurements of the osmotic pressure, from which the molecular weight is subsequently calculated. Although it is not usual to determine molecular weight by direct measurement of the osmotic pressure and vapour tension, yet in view of the simplifications which have been introduced into the methods of effecting these determinations, they will be considered here along with the more usual methods, of raising of the boiling point, and lowering of the freezing point. They are considered more on account of their instructive nature than on account of the accuracy of the results, although these, with due care, are quite equal to those obtained by the other methods.

1. Determination of Osmotic Pressure

When a solvent and a solution of a substance in that solvent are separated by a semipermeable membrane, *i.e.* a medium through which the molecules of the solvent can pass, but not those of the dissolved substance, the solvent will pass through the medium into the solution, tending to make the concentration of the dissolved substance the same on both sides of the membrane. Should the solution be enclosed in a vessel of constant volume, the pressure inside the vessel must, of necessity, increase as the solvent enters it. After the solvent has passed in for some time, a condition of equilibrium is set up, at which the amount of solvent passing through the membrane is the same in both directions. This point is reached when the pressure inside the vessel is the same as the osmotic pressure. If, then, the pressure in the vessel at the equilibrium point can be determined, the osmotic pressure will be known.

There are three main difficulties which stand in the way of the general adoption of the measurement of osmotic pressure for obtaining molecular weights: 1. the position of equilibrium is reached only very slowly; 2. the pressures generated are very great, and, in the case of even moderately concentrated solutions, often burst the membrane; 3. perfectly semipermeable membranes have never been obtained; the membranes generally in use always allow some of the dissolved substance to pass through. For the present purpose, however, using dilute solutions, no great pressure will be generated, and consequently there will be no great danger of bursting the membrane, and the error due to the imperfections of the semipermeable medium can be neglected.

Preparation of a Membrane. Copper ferrocyanide is one of the best semipermeable membranes for aqueous solutions; this is best prepared by depositing it in the pores of an unglazed earthenware vessel. Such a vessel as is used in Daniell cells serves excellently. The pot is first of all soaked in water in a vacuum, to remove all the air from the pores, and then, whilst still wet, it is filled to within 2 cm. of the top with a 1 per cent. solution of copper sulphate, and placed in a beaker containing a solution of potassium ferrocyanide of similar strength. The liquid outside the pot must be at the same height as that inside. The two liquids diffuse into the walls of the pot, and meet midway between the two surfaces, with the formation of cupric ferrocyanide. The solutions should be left in contact for about six hours; the pot is then washed out with water to remove all salts, both from the inside and the outside. The top of the cell, which has not been in the solutions, is then dipped into a dish of molten paraffin wax, and when this has set, the cell is ready for use.

Membranes of greater durability may be made by a method due to Morse and Horn (*Am. Chem. Journ.* 1901, 80). The porous pot is filled with a 5 per cent. solution of potassium sulphate, and placed in a beaker containing the same solution, and an electric current, driven by about 100 volts, is passed through from the beaker to the porous pot by means of platinum electrodes. A strong endosmosis takes place in the direction of the current, so that the solution passes from the beaker into the cell and sweeps with it all air contained in the walls. The excess liquid in the cell must be constantly removed by means of a pipette. The current is allowed to pass until about 300 c.c. of solution have passed through the walls. The pot is then thoroughly soaked in distilled water, repeatedly changed, until the water which has been used for washing, gives no precipitate with barium chloride. The pot is then filled with a tenth normal solution of potassium ferrocyanide, and placed in a beaker containing a tenth normal solution of copper sulphate. The porous pot is surrounded with a wide strip of copper foil which reaches from the top to the bottom of the cell and serves as the positive electrode. The negative electrode is a platinum wire which is placed inside the porous pot and reaches to the bottom. A current driven by about 100 volts is then passed, and the $Fe(CN)_6^{\text{iv}}$ ions, travelling toward the anode, will meet the $Cu^{\cdot\cdot}$ ions, travelling toward the cathode, in the middle of the walls of the porous pot, and a precipitate of cupric ferrocyanide will be formed there. After a few minutes the resistance of the cell to the passage of the current rises enormously, and this serves as a test for an unbroken membrane. If the membrane is intact, no copper will reach the inside of the porous pot, and no ferrocyanide the outside. By using membranes made in this way, Berkeley and Hartley have measured osmotic pressures amounting to several tons to the square inch. Having deposited the membrane, wash the pot carefully inside and out, and wax the top as described before.

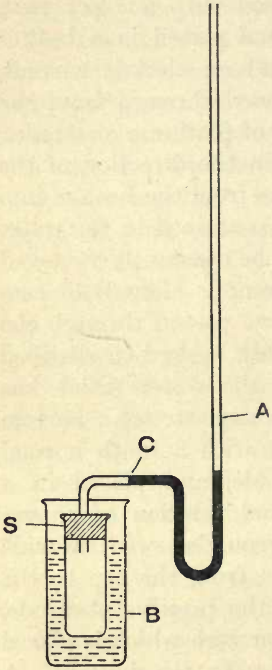

Fig. 32.

Method of Measurement. The porous pot containing the membrane should be washed out with the solution to be measured, and then almost filled with the same solution. A well fitting stopper S (Fig. 32) carrying a manometer tube A of about 5 mm. bore, is tightly pressed in, so that no air bubbles remain in the pot, and the liquid reaches not further than the point C in the tube. The stopper and joint are then dried and coated with paraffin wax. Mercury is then run into the manometer tube so that it closes off and defines the volume of the solution. This must be kept constant throughout the experiment. The porous pot is then placed in a beaker B, in a thermostat, and when the porous pot and its contents have assumed the temperature of the bath, a mark is made to indicate the position of the solution in the tube A. The level of the mercury is then made the same in both sides of the gauge, and distilled water is poured into the beaker so that it entirely covers the porous pot. The volume of the liquid will tend to increase, due to osmosis, and must be kept back by the addition of mercury to the open limb of the manometer. When the position of equilibrium has been set up, which may require several days, the pressure is read off, and represents the osmotic pressure of the solution. If p be the osmotic pressure, t the temperature of the experiment, and w the weight of substance dissolved in v c.c. of the solution, then, since the volume of the solution represents the volume occupied by the dissolved molecules, it can be treated exactly as though it is the volume of a gas. Hence

$$V_0 = v \cdot \frac{273}{273+t} \cdot \frac{p}{760}.$$

The corrected volume V_0 contains w grams of the dissolved substance. Hence,

$$22{\cdot}40 \text{ litres will contain } \frac{w \times 22400}{V_0},$$

and this number is the molecular weight of the dissolved substance.

In the case of solutions of electrolytes, the osmotic pressures are larger, and the calculated molecular weights smaller than those demanded by the simplest possible chemical formulae. These discrepancies are due to the electrolytic dissociation of the dissolved substances. If P be the osmotic pressure obtained experimentally, and P_1 that calculated on the assumption that the dissolved substance has the simplest possible formula, and if i represent the degree of dissociation of the dissolved substance, and n the number of ions into which one molecule dissociates, then $1:1+i(n-1)$ represents the ratio of the number of molecules which would have been present had no dissociation occurred, to the number which are actually present. This ratio is the same as the corresponding osmotic pressures, *i.e.*

$$\frac{1}{1+i(n-1)}=\frac{P_1}{P} \text{ or } i=\frac{P-P_1}{P_1(n-1)}.$$

EXPERIMENTS

(i) *Determine the Osmotic Pressure of Cane Sugar, and calculate its Molecular Weight.* Make up a litre of cane sugar solution containing about 2 grams, weighed to the nearest milligram. Prepare a porous pot of about 6 cm. diameter and 20 cm. height by one of the methods described above. Rinse the pot out two or three times with the sugar solution. Then fill it, and put the apparatus together as described above, and place it in a beaker in a thermostat. This experiment will take several days to complete, so it is wise to use a large vessel of water at the laboratory temperature as thermostat; this allows of the experiment being left to stand in some out-of-the-way corner, without inconvenience. When the temperature has become constant, fill the beaker with distilled water, and adjust the mercury in the manometer. Then add mercury, from time to time, to the open end of the manometer until the pressure remains constant. Make the necessary observations of pressure and temperature, and calculate the molecular weight by the formula given above.

(ii) *Determine the Osmotic Pressure and Degree of Dissociation of Potassium Chloride.* Use a solution of potassium chloride containing about 1 gram per litre, for this experiment.

2. Determination of Vapour Tension

When a substance is dissolved in a solvent, the vapour pressure of the solution is lowered by an amount which depends on the relative quantities of the solvent and the dissolved substance. Equimolecular quantities of all substances, dissolved in the same volume of a given solvent, lower the vapour pressure by the same amount. The relative lowering of the vapour pressure is equal to the ratio of the number of dissolved molecules and the total number of molecules in the solution.

Thus, if p' be the vapour pressure of the solvent at a given temperature, and p that of the solution at the same temperature, and if g be the weight of the substance dissolved in G grams of the solvent, m the molecular weight of the dissolved substance, and M that of the solvent, then since $\frac{g}{m}$ and $\frac{\mathsf{G}}{\mathsf{M}}$ represent the number of molecules of the dissolved substance and solvent respectively,

$$\frac{p'-p}{p'}=\frac{\frac{g}{m}}{\frac{g}{m}+\frac{\mathsf{G}}{\mathsf{M}}}.$$

Should all the factors in the above expression except m be either known or easily determinable, it is obvious that molecular weights of substances in solution may be obtained by its means.

The direct determination of the change in vapour pressure could be effected by passing a small quantity of the solvent up a barometer tube, and noting the depression of the mercury, and then repeating the experiment with the solution. This method, however, is seldom employed, for the following reasons: 1. the amount of lowering of the vapour pressure is very small, and consequently the results will be correspondingly inexact; 2. traces of volatile impurity make great differences in the results.

A method by which the vapour tension may be indirectly measured was suggested by Ostwald, and improved by Will and Bredig. If air is bubbled through a liquid, it takes up a quantity of the vapour of that liquid which is proportional to the vapour tension. Consequently, if equal quantities of dry air were bubbled respectively through the solvent and the solution, and the vapour extracted from both by suitable drying agents, two quantities of the solvent would be obtained whose weights would be in the same ratio as the vapour tensions of the solvent and the solution. If, on the other hand, the air is bubbled first through the solution and then through the solvent, it will take up an amount of the solvent from the solution proportional to its vapour pressure, and from the pure solvent a further amount, proportional to the difference between the vapour tensions of the solution and the pure solvent. If, then, the vessels containing the solvent and the solution are weighed before and after the current of air has been passed through them, the differences in the weights will give the ratio of the vapour tensions. If p be the vapour tension of the solution and p' that of the solvent, then,

$$\frac{\text{The loss of weight of the solution}}{\text{The loss of weight of the solvent}}=\frac{p}{p'-p}.$$

It has already been shown that

$$\frac{p'-p}{p'}=\frac{\frac{g}{m}}{\frac{g}{m}+\frac{\mathrm{G}}{\mathrm{M}}}.$$

Hence, $$\frac{\text{Loss of weight of the solvent}}{\text{Loss of weight of the solution}} = \frac{\frac{g}{m}}{\frac{\mathsf{G}}{\mathsf{M}}},$$

and $$m = \frac{g}{\mathsf{G}} \cdot \mathsf{M} \cdot \frac{\text{Loss of weight of the solution}}{\text{Loss of weight of the solvent}}.$$

EXPERIMENT

Determine the Molecular Weight of Cane Sugar. The apparatus required for this experiment consists chiefly of six sets of Liebig's potash bulbs. Three of these contain the solution, and the other three the pure solvent. Fill three of the bulbs with a solution of cane sugar, whose concentration is accurately known, and which contains about 17 grams per litre; the other three bulbs must be filled with distilled water. After weighing, connect them together as illustrated in Fig. 33, using thick-walled rubber tubing, which must be wired on. The air may be supplied from a gas-holder, or it may be drawn through the apparatus by means of a water pump; it must, however, be thoroughly dried by calcium chloride and sulphuric acid before it enters the bulbs. Since the vapour tension changes with temperature, the bulbs must be placed in a thermostat, and the air raised to the same temperature by circulating it through a long coil of lead tubing immersed in the same thermostat. Whichever way the air is passed through, it must always enter the solution before it enters the pure solvent; it must be bubbled through at the rate of 2–3 bubbles per second, and continued for about 90 minutes. It is advisable, in this experiment, to attach two weighed calcium chloride tubes to the end of the row of bulbs, and thus absorb all the moisture from the air as it escapes. This will furnish a control to the experiment, for the increase in the weight of the calcium chloride tubes ought obviously to be equal to the total loss of weight of the bulbs. A large vessel of water which has been standing in the laboratory for several hours will not change its temperature appreciably while the experiment is being carried out, and will serve admirably as a thermostat for this experiment. Use the formula given above in the calculation of the results of the experiment.

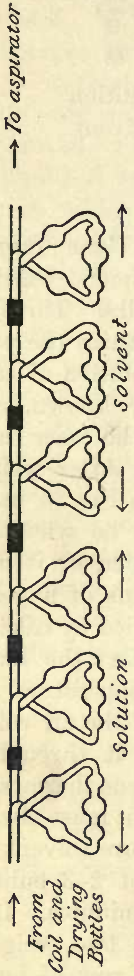

FIG. 33.

3. Boiling Point Method

It has already been noted that when a substance is dissolved in a solvent, the vapour tension is lowered. The boiling point of a liquid is defined as that temperature at which the vapour tension of the liquid becomes equal to that of the surrounding atmosphere, hence if the vapour tension of a liquid is lowered by dissolving a non-volatile substance in it, it follows that the boiling point of such a solution will be higher than the boiling point of the pure solvent. The increase in the boiling point will be proportional to the vapour tension, and consequently, also proportional to the amount of substance dissolved in the solvent. If w grams of a substance of molecular weight m dissolved in W grams of the solvent raises the boiling point t°, then the molecular weight of the dissolved substance is given by the expression

$$m = \mathrm{K} \cdot \frac{100w}{\mathrm{W}t},$$

where K is a constant, known as the molecular raising of the boiling point, *i.e.* it represents the number of degrees by which the boiling point of a given solvent will be raised, if one gram molecular weight of any substance is dissolved in 100 grams of the solvent. The value of K may be determined experimentally, by measuring the amount which the boiling point of a given solvent is raised by the solution of a known weight of a substance of known molecular weight in it. Thus, if 5 grams of nitrobenzene are dissolved in 25 grams of benzene, and the boiling point is raised 4°·272, then the value of K is given by

$$\mathrm{K} = \tfrac{25}{100} \times \tfrac{123}{5} \times 4{\cdot}272 = 26^{\circ}{\cdot}7,$$

where 123 is the known molecular weight of nitrobenzene.

The value of K can also be obtained from theoretical considerations, from the latent heat of vaporisation of the solvent:

$$\mathrm{K} = \frac{0{\cdot}02\mathrm{T}^2}{\mathrm{L}},$$

in which T is the boiling point of the solvent in absolute measure, and L is the latent heat of vaporisation. A list of the more common solvents is given below, together with the values of K and the latent heat of vaporisation.

The method and apparatus generally adopted for the determination of the molecular weight by the raising of the boiling point, is due to Beckmann, and can be suitably described here. The apparatus consists of a boiling tube A (Fig. 34) about 15 mm. diameter, fitted near the top with a wide side tube B. The side tube is fitted with a cork carrying a spiral air condenser **C**, or a small water condenser. The boiling tube fits loosely into a double-walled glass jacket **D**, which is also fitted with a side tube and condenser **E**. This jacket contains a quantity of the solvent, which is kept boiling during a determination, and thus surrounds the boiling tube **A** with a vapour at about its own temperature, and effectually prevents loss of heat by radiation. A Beckmann thermometer **T** passes through a cork in the top of **A**, and reaches almost down to the bottom. The heating jacket and boiling tube rest on an asbestos box **F**, fitted with two chimneys **G** which serve to convey the hot air from underneath the box past the apparatus, and so prevent local superheating. The box **F** is made as

Solvent.	K.	Boiling Point.	Latent Heat of Vaporisation
Water, - -	5·20	100°	535·9
Ether, - -	21·0	35°	90·0
Chloroform, -	36·6	61°·2	58·5
Ethyl Alcohol, -	11·5	78°·8	215·0
Acetone, - -	17·0	56°·3	125·3
Benzene, - -	27·0	80°·3	92·9
Aniline, - -	32·2	184°	93·3
Pyridine, - -	29·8	115°	104·0

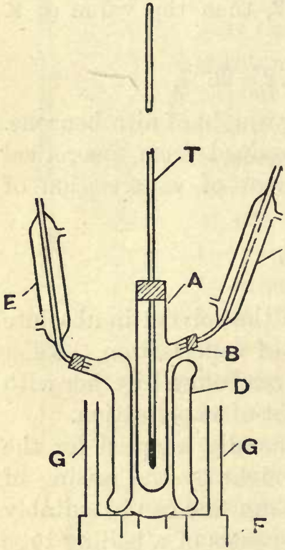

Fig. 34.

indicated in Fig. 34, and consists of two concentric rings of asbestos, the smaller one being fitted into a hole in the top of the box, which is covered by a piece of wire gauze, and this in its turn by asbestos fibre. The heating of the apparatus is effected by two bunsen burners, which are placed at the corners of the box opposite the chimneys.

Before proceeding to describe the method of carrying out a determination, a short description of the Beckmann thermometer is necessary. A moment's consideration will make it clear that, if it is desired to determine molecular weights by the method of raising of the boiling point, to within 1 or 2 per cent. accuracy, it will be necessary to measure the boiling point of the solution to within 0°·001 or 0°·002. Obviously a thermometer graduated in 0°·001 to read over any long range of temperature would be so very long as to be quite unusable. The Beckmann thermometer overcomes this difficulty, by having a bulb in which the amount of mercury may be varied.

The thermometer is generally made, graduated over about six degrees, divided in tenths and hundredths of a degree; the bulb is large, and at the other end of the capillary a small reservoir is attached (see Fig. 35) into which a portion of the mercury may be driven if the thermometer is required for high temperatures, and from which more mercury may be withdrawn if the thermometer is required for low temperatures. A Beckmann thermometer, there-

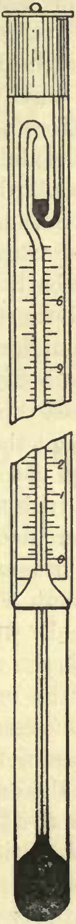

FIG. 35.

fore, serves the same purpose as a series of very accurate thermometers which have different ranges. The same Beckmann thermometer cannot, however, be used over very wide ranges of temperature, *e.g.* for the boiling and freezing points of water, it is usual to have a series of them with ranges of about 60°. Before using a Beckmann thermometer the divisions on its scale should be calibrated by comparing them with a standard thermometer. This is best done by placing the two thermometers side by side in a liquid bath and very slowly raising the temperature, noting the readings of both at each division. Having calibrated the scale, the thermometer must be "set" for the particular experiment for which it is to be used. For use in a raising of the boiling point determination, the mercury in the bulb must be so adjusted that the thread is stationary at about the first degree division, at the boiling point of the liquid to be used. This will allow the boiling point to be raised about 5 degrees. The adjustment of the mercury in the bulb is achieved by placing the Beckmann thermometer, along with another thermometer, in a bath about 6° above the boiling point of the solvent to be used. If the mercury thread at this temperature just fills the whole of the capillary, without forming a globule in the reservoir, the thermometer is correctly set. If, on the other hand, as is usually the case, the thread either does not entirely fill the capillary, or forms a globule at the end in the reservoir, mercury must be added to, or removed from, the bulb. First assume the capillary is not entirely filled; under these circumstances the temperature of the bath must be raised until the capillary is entirely filled and a small globule is formed in the reservoir, then the thermometer is quickly reversed and given a sharp downward jerk, whereby the mercury in the reservoir is joined to the thread. The thermometer is then placed in the bath, without shaking, and cooled down to a temperature about 6° above the boiling point of the solvent to be used. Then the thermometer is removed from the bath and again given a sharp downward jerk, which has the effect of breaking off the mercury still in the reservoir, from the thread. The thermometer should, then, be "set," but it must be tested by placing it in a bath at the boiling point of the solvent; if the thread now stands not higher than the second degree division it is correctly "set." Next assume that the thermometer bulb originally contains too much mercury, in this case it is treated as in the latter part of the above description.

Should the thermometer be required for a lowering of the freezing point determination, it must be "set" so that the thread stands within one degree of the top of the scale, at the freezing point of the solvent. This will allow of the measurement of about 5 degrees lowering. To "set" the thermometer in this case, the procedure is exactly as described above; the thermometer is placed in a bath about 3 degrees above the freezing point of the solvent and treated exactly as in the case of "setting" for boiling point determinations. Beckmann thermometers should not be used for twenty-four hours after they have been "set." Having adjusted the thermometer for the experiment, the boiling tube, which has a stout platinum wire fused into the bottom, is fitted with two corks, and weighed, then about 20 c.c. of the solvent are introduced and it is re-weighed. The thermometer is then inserted, and a quantity of small garnets, which have been previously washed with the solvent and well dried, are introduced through the side tube, and shaken into position so that they entirely cover the bulb of the thermometer. The object of adding the garnets is to ensure regular ebullition. The tube is then placed in the heating jacket, which contains about 25–30 c.c. of the solvent and a quantity of beads, again to prevent bumping. The condensers are then placed in position and the heating commenced. The flames should be protected from draughts, and the ebullition in the outer jacket fairly brisk and regular, so that the liquid flows from the condenser at the rate of about one drop in five seconds, otherwise the thermometer will register a fluctuating temperature. The boiling point of the pure solvent must first be determined; the temperature will continue to rise for a considerable time after boiling has commenced, and it may be quite half an hour before it becomes stationary. The final reading of the temperature should only be taken after it has been stationary for about five minutes. Before reading a Beckmann thermometer, the top should always be tapped with the finger, this is because long fine threads of mercury, like the thread of the Beckmann thermometer, are apt to stick, and the tapping has the effect of removing this source of error. When the boiling point of the solvent has been determined, the flames are turned out, and, as soon as the liquid ceases to boil, the condenser attached to the boiling tube is removed, and a weighed quantity of the substance whose molecular weight is to be determined is added through the side tube. The condenser is then replaced and the boiling point re-determined. Further quantities of the substance are then added, and the boiling points corresponding to them determined in the same way. The molecular weight should now be calculated for each temperature, the total weight of dissolved substance present when the temperature is taken, being used in the calculation. It is often recommended that a quantity, 0·2 gram, should be deducted from the total weight of the solvent present, to allow for the solvent remaining in the condenser and side tube. Such a deduction is purely arbitrary and ought not to be made, because the experimental error is always more than would be accounted for by 0·2 gram of the solvent remaining in the side tube, and this figure rarely represents the quantity retained by the condenser, for different condensers obviously retain different amounts. It is essential that the barometric pressure should be noted at the beginning and at the end of an experiment, and, if it is found to have changed, the boiling points should be corrected to correspond.

Attention may be called here to the fact that acetone is an excellent solvent for these determinations, since it dissolves so many substances which are not at all, or only sparingly, soluble in most other solvents, and further, it can easily be obtained quite pure.

Form in which Substances are Introduced. The substances, if solids, should be finely powdered and placed in a tube, about 14 cm. long and 5 mm. wide, closed at one end, in which they are weighed. This tube can then be placed right into the side tube of the boiling tube, and a quantity of the substance shaken in by gently tapping the weighing tube, the weight added being obtained by difference. It often happens, however, in this method of introducing the substance, that portions of it remain in the side tube and have to be washed down by the solvent as it flows back from the condenser. This often takes considerable time, and tends to unduly prolong the experiment; it can, however, be avoided by introducing the substance as a tablet. Such tablets are made by compressing the substance in a press which is sold for the purpose. These tablets are hard, and can easily be handled with a pincette. Another method of introducing the substance is to melt a quantity of it in a thin-walled glass tube, into a stick. This stick or pencil can easily be removed from the tube and broken into pieces of suitable length, which can then be weighed and added to the solvent by means of a pincette.

If the substance to be added is a liquid, it is introduced by means of a pipette shaped as in Fig. 36, which has a long delivery tube. The pipette is filled with the liquid and weighed; the delivery tube is then inserted right inside the side tube of the boiling tube, and a small quantity of the liquid blown out of the pipette. If a drop of liquid remains hanging on the point of the pipette, it is removed by touching it against the side of the thermometer.

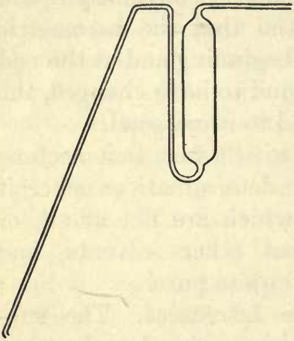

FIG. 36.

It is especially important to note that the molecular weight of substances which have an appreciable vapour pressure at the boiling point of the solvent, should not be determined by this method. Generally the substance must have a boiling point at least 120° higher than the boiling point of the solvent.

Abnormal Molecular Weights. It often happens that the molecular weight of a substance obtained by the methods described in this section, is either larger or smaller than is demanded by the simplest possible formula of the substance. This is due, in the former case, to an association of the molecules taking place, and in the latter case, to a dissociation. Certain solvents have an associating tendency, viz. those which do not contain an hydroxyl group, such as benzene, chloroform, carbon bisulphide, etc.; those which contain an hydroxyl group, such as water and the alcohols, have a dissociating tendency. It is possible to determine the degree of association or dissociation of substances in solution, from the values obtained as the molecular weight.

If M be the calculated molecular weight of a substance and M_1 that experimentally determined, and if a represent the degree of association, and n the number of simple molecules which associate to form a complex molecule, then the ratio of the number of molecules actually present to the number which would be present had no association taken place, is given by $1-a+\frac{a}{n}:1$. This has the same value as the ratio between the experimentally determined and the calculated molecular weight, *i.e.* $M : M_1$, or

$$\frac{M_1}{M}=\frac{1}{1-a+\frac{a}{n}} : a=\frac{M_1-M}{M_1\left(1-\frac{1}{n}\right)}.$$

For dissociated substances, if d be the degree of dissociation and n the number of parts into which one molecule dissociates, and M and M_1 have the same significance as before, then the ratio between the number of molecules present to the number which would have been present had no dissociation taken place, is given by $1:1-d+nd$, and this is the same as the ratio between the observed and the calculated molecular weight, *i.e.* $M_1 : M$;

$$\frac{M_1}{M}=\frac{1}{1-d+dn}, \quad \text{or} \quad d=\frac{M-M_1}{M_1(n-1)}.$$

EXPERIMENTS

(i) *Determine the Molecular Weight of Azobenzene in Ethyl Alcohol Solution.* The experiment must be carried out exactly as described above. Use about 20 c.c. of absolute alcohol, and add the following quantities of azobenzene successively to it, 0·1, 0·1, 0·2, 0·2 and 0·5 gram.

(ii) *Determine the Degree of Association of Nitrobenzene in Benzene Solution.* In this experiment, quantities of about 0·1, 0·2, 0·5, 1·0 and 2·0 grams should be added to about 20 c.c. of benzene, and the degree of association calculated for each case, on the assumption that two single molecules associate to form one complex molecule.

(iii) *Determine the Degree of Dissociation of Potassium Iodide in Water Solution.* Quantities of about 0·2, 0·2, 0·4, 1·0 and 1·0 gram should be added successively, to about 20 c.c. of water. The influence of concentration on the degree of dissociation should be indicated by plotting the degree of dissociation against the concentration of the solution.

(iv) *Determine the Molecular Rise of the Boiling Point and the Latent Heat of Vaporisation of Acetone.* For this experiment, use about 0·5 gram of azobenzene and 20 grams of acetone. The molecular weight of azobenzene in acetone solution may be assumed to be that of the simple chemical formula.

Other Boiling Point Methods. For chemical purposes, a method of determining molecular weight which will give the values to within 5 per cent. is sufficiently accurate, for in most cases the values are only used to decide whether the empirical formula or a multiple of it, represents the molecular weight of the substance in question. For this purpose, a method due to Landsberger and modified by Walker and Lumsden is quite suitable. It possesses many advantages over the Beckmann method, the chief of which is the rapidity with which the determinations can be carried out. One quantity of substance only, has to be weighed out, and a series of readings are obtained by varying the amount of the solvent used, which is measured, not by weight, but by volume.

The apparatus, as devised by Walker and Lumsden, consists of a graduated tube A (Fig. 37), which is blown

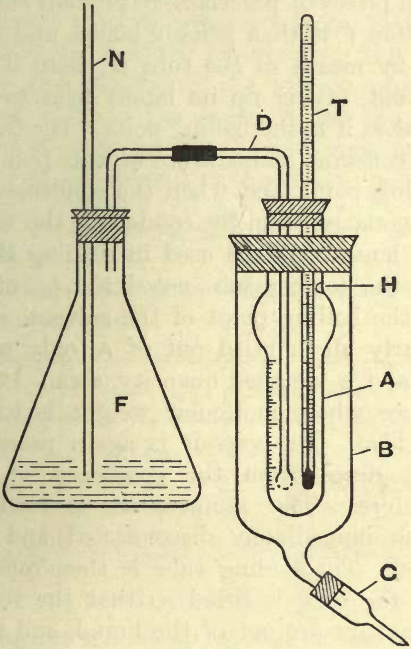

Fig. 37.

into a bulb above the graduations, and has a small pinhole H pierced in it above the bulb. This tube is fitted with a two holed rubber stopper, which carries a thermometer T graduated in twentieths of a degree, and a narrow tube D which reaches to the bottom of the tube, and is terminated by a small bulb perforated by several small holes. The boiling tube A is supported in a glass jacket B which is connected to a condenser C. The tube D is connected to a conical flask F fitted with a safety tube N.

To carry out a determination, about 10 c.c. of the solvent are placed in A, and about 150 c.c. in F, together with several pieces of porcelain, to prevent superheating. The solvent in F is then briskly boiled, and the vapour led into A by means of the tube D; here it is at first condensed, but, giving up its latent heat to the liquid in A, soon raises it to the boiling point. The thermometer indicates a constant temperature at this point, viz. that of the boiling point, and when the condensed liquid is dropping regularly, from the condenser, the temperature is read. A lens should be used in reading the thermometer, and the temperature noted to $\frac{1}{100}$ of a degree. This gives the boiling point of the solvent. The liquid is then nearly all emptied out of A, only about 3 c.c. being left, and a weighed quantity, about 1·5 grams, of the substance whose molecular weight is to be determined is added. The vapour is again passed in until the solvent drops from the condenser at the same rate as before. The temperature is read, and the boiling flask immediately disconnected and the flame extinguished. The boiling tube is then removed from the jacket, the cork is lifted so that the thermometer and delivery tube are out of the liquid, and the volume is read to the nearest tenth of a cubic centimetre. Now, the various parts of the apparatus are replaced, and the vapour again passed in as before, and a second reading obtained. If the volume of liquid admits, a third reading should be taken.

The molecular weight is calculated by the same formula as used in the case of the Beckmann method; the constant K', however, has a different value;

$$m = K' \frac{100w}{Vd},$$

where m is the molecular weight, w the weight of the substance added, V the volume of solvent, d the increase in the boiling point, and K' the constant.

This constant may be obtained from that employed in the Beckmann method, by dividing the Beckmann constant by the density of the solvent at the boiling point. Thus, if K is the constant for the Beckmann method, and K' that for the Landsberger method, and s the density of the solvent at the boiling point, then

$$K' = \frac{K}{s}.$$

The following table gives the constants for a few of the commoner solvents:

Solvent.	K'.	Boiling Point.	Latent Heat of Vaporisation.
Ethyl Alcohol, -	15·60	78°·8	215
Ether, - - -	30·30	35°	90
Acetone, - -	22·20	56°·3	125·3
Water, - -	5·40	100°	535·9
Carbon Bisulphide,	19·30	46°·2	86·7

In choosing the solvent to be used in this method, two points must be observed: 1. the latent heat of vaporisation must be as large as possible, so that the temperature of the solvent in the boiling tube may be brought up to the boiling point as quickly as possible; 2. the molecular elevation must be as large as possible, to make it possible to read the temperature difference with sufficient accuracy, by the type of thermometer employed. Water is not a good solvent for this method, although it has such a large latent heat of vaporisation, because its molecular elevation is so small, but it may be used if sufficiently large quantities of dissolved substance are used. Alcohol and ether are the best solvents for this method of determination.

EXPERIMENTS

(i) *Determine the Molecular Weight of Anthracene in Ethyl Alcohol Solution.* Use about 1·5 grams of anthracene for this experiment.

(ii) *Determine the Degree of Dissociation of Potassium Iodide in Water Solution.* Use about 2 grams of potassium iodide, and calculate the degree of dissociation by the method described above.

(iii) *Determine the Molecular Weight of Benzamide in Water Solution, and calculate the Degree of Association.* Use about 2 grams of benzamide for the experiment. Calculate the degree of association on the assumption that two single molecules of benzamide associate to form one complex molecule.

Many modifications of the Walker-Lumsden apparatus have been described, among which those due to Sakuri (*J.C.S.* 1892, 989) and Ludlam (*J.C.S.* 1902, 1194) may be mentioned here.

The apparatus due to Ludlam possesses many points in which it is superior to the others, and it will not be out of place to describe it here. Chief among its advantages are the great reduction in the size of the apparatus, the speed with which the determinations can be effected, and the large number of readings which can be obtained with one quantity of substance, *e.g.* with carbon bisulphide as the solvent, as many as seven readings have been obtained.

The apparatus consists of a flask F (Fig. 38), about 300 c.c. capacity. The flask has a wide neck to which a side tube S is attached, this serves for the introduction of the solvent. The flask F is fitted with a large cork carrying a tube B, 10 cm. long and 2·5 cm. diameter, which has a small hole H pierced in its side. B is fitted with a cork, and carries a graduated tube C, which is perforated at the bottom by a small hole D. This hole is closed by a glass pellet E which serves as a valve, and is kept in position by a piece of platinum wire K. The top of the tube C is shaped as indicated in the diagram, and is fitted with two side tubes, M and N. The side tube M is used for introducing the substance, and the tube N is attached to a condenser. A thermometer, registering tenths of a degree, is used with this apparatus. The side tube S is closed by a rubber stopper which carries a glass tube closed by a piece of rubber tubing and a clip X.

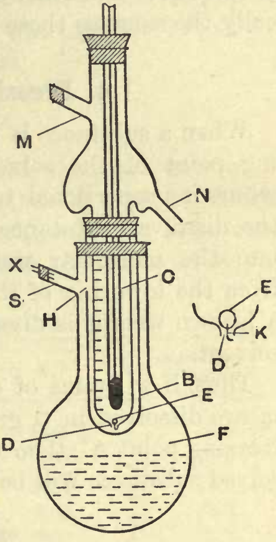

FIG. 38.

To make a determination, the flask F is half filled with the solvent, to which a few pieces of broken porcelain are added to prevent superheating. A small quantity of the solvent, about 3 c.c., is placed in C, and the heating commenced. The liquid in F boils, and the vapour passes through the hole H and down the space between B and C, thus forming a double vapour bath, which effectually prevents the temperature of the liquid in C being influenced by the outside temperature. The vapour then passes through the valve E and through the liquid. The other details of this method are practically the same as those of the Walker-Lumsden method.

4. Freezing Point Method

When a substance is dissolved in a solvent, the freezing point of the solvent is depressed by an amount which is proportional to the molecular concentration of the dissolved substance. Hence it is possible to calculate the molecular weight of the dissolved substance from the lowering of the freezing point, produced when a known weight is dissolved in a known weight of the solvent.

Thus, if w grams of a substance of molecular weight m are dissolved in G grams of a solvent, and lower the freezing point $\Delta°$, then the molecular weight of the dissolved substance will be given by the expression

$$m = \mathrm{K}\frac{100w}{\mathrm{G}\Delta},$$

where K is a constant depending on the solvent and known as the "molecular depression," *i.e.* the amount by which the freezing point of the solvent would be lowered if one gram molecular weight of a substance was dissolved in 100 grams of the solvent.

The value of K for any particular solvent can be found by determining the lowering of the freezing point produced by a known weight of a substance of known molecular weight. Thus, if a grams of a substance of molecular weight M were dissolved in W grams of a solvent, and lowered the freezing point $t°$, then the value of K would be given by the expression

$$\mathsf{K} = \frac{\mathsf{W}}{100} \cdot \frac{t}{a} \mathsf{M}.$$

The constant may also be calculated from the latent heat of fusion of the solvent, in a way similar to that in which the boiling point constant was calculated from the latent heat of vaporisation. Thus,

$$\mathsf{K} = \frac{0{\cdot}02\mathsf{T}^2}{\mathsf{L}},$$

where T is the freezing point of the pure solvent in absolute measure, and L is the latent heat of fusion. The accompanying table gives a few of the more commonly used solvents, together with the value of K and the latent heat of fusion.

Solvent.	Freezing Point.	K.	Latent Heat of Fusion.
Water, - -	0°	18·6	79·1
Acetic Acid, -	17°	39·0	43·1
Benzene, - -	5°·5	50·0	30·1
Nitrobenzene, -	6°·0	70·0	22·3
Benzophenone, -	48°·1	98·0	23·7
Azobenzene, -	69°	83·0	27·9

The method of the lowering of the freezing point can only be employed for the determination of molecular weights when, in the process of freezing, the solvent separates out alone. Hence, in the case of those substances which form mixed crystals or isomorphous mixtures with the solvent, the method is inapplicable.

In everyday practice, it is usual to employ solvents which are liquid at ordinary temperature, and cause them to freeze by immersion in cooling baths; it is, however, often advantageous to employ as solvents, substances which are solid at the ordinary temperature, and to melt them by surrounding them with a bath just above their melting point, and then allow them to freeze by lowering the bath to just below their melting point. The method of working is exactly the same for both classes of solvents, but it will be well to consider them separately.

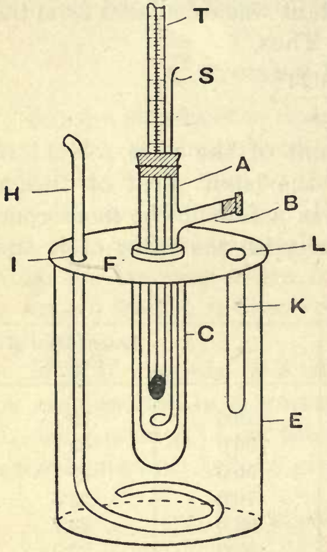

Fig. 39.

1. Solvents which are Liquid at Ordinary Temperature. The apparatus employed for determining the lowering of the freezing point by means of this class of solvent, consists of a glass tube A (Fig. 39), about 14 cm. long and 2 cm. wide, which is fitted with a side tube B. The tube A is supported by means of a cork in a second, slightly wider, glass tube C, which serves as an air jacket and prevents the freezing tube A from coming into direct contact with the cooling mixture, and thereby ensures slower and more regular cooling of the contents of A. The freezing tube is fitted with a cork, through which pass a Beckmann thermometer T and a stirrer S. The whole apparatus is supported in a suitable freezing mixture, which is contained in a stout glass jar

E, fitted with a metal lid L, into which three holes are bored. The centre hole F carries the freezing tube with its air jacket, a metal stirrer H passes through one of the smaller holes, and the other supports a test tube K, which contains a small quantity of the solvent used in the experiment.

Before commencing an experiment, the Beckmann thermometer must be adjusted, as described in the last section, so that it will record the temperatures of the experiment. The freezing tube A is fitted with two unbored corks and weighed, 15–20 grams of the solvent are then added, and the tube weighed again. The weighings of the solvent, in determinations of this type, need only be made to the nearest centigram. The thermometer and stirrer are then placed in the tube, so that the bulb of the thermometer is completely immersed in the solvent. The freezing tube is then placed in the air jacket, and the whole immersed in the cooling bath, which should have a temperature about 2°–3° below the freezing point of the solvent. Having weighed the solvent and fitted up the apparatus, an approximate determination of the freezing point should first be taken. This is done by removing the freezing tube from the air jacket and immersing it directly into the freezing mixture until crystals of the solvent begin to form. When this happens, the tube is removed from the freezing bath, dried quickly, and placed in the air jacket which is still in the freezing mixture, and stirred slowly, the point at which the temperature remains constant being noted. The freezing tube is then removed from the air jacket, and the frozen solvent melted by holding it in the hand. Then it is replaced in the air jacket and slowly stirred until the temperature is about 0°·2–0°·5 below the approximate freezing point found above; then it is stirred more rapidly; the solvent will now generally commence to solidify, and the temperature will rise. It must be stirred slowly as long as the temperature rises, care being taken to tap the thermometer, and so prevent the thread hanging, before taking a reading. The highest point reached is then noted as the freezing point of the solvent. The operation must be repeated until three determinations have been obtained, which agree to within 0°·002. The mean of the three readings is taken as the freezing point of the solvent. If, as not infrequently happens, the solvent refuses to solidify when cooled to 0°·5 below its freezing point, solidification can be induced by adding a tiny crystal of the solvent from the tube **K**. On no account should the liquid be supercooled more than 0°·5, otherwise the freezing point registered by the thermometer will be inaccurate. When the freezing point of the pure solvent has been obtained, the freezing tube is removed from the cooling bath, and about 0·1–0·2 of the substance is added through the side tube **B**; in the case of solids this is added as a tablet or stick, and in the case of liquids by means of a pipette (see last section). The solvent is stirred until all the substance has dissolved, and then the tube is replaced in the air jacket and cooled again, with constant slow stirring, and the new freezing point determined exactly as in the case of the pure solvent. Here again three concordant readings must be obtained. Further quantities of the dissolved substance may then be added, and still greater lowerings obtained.

Abnormal molecular weights are often obtained by this method, just as in the case of the boiling point method, due to association or dissociation of the dissolved substance. The degree of association or dissociation can be calculated from the molecular weights obtained from the freezing point lowering, by using formulae similar to those given in the last section.

EXPERIMENTS

(i) *Determine the Molecular Weight of p-Toluidine in Benzene Solution.* A cooling bath of ice and water must be used for this experiment. Add successive quantities of 0·2, 0·2 and 0·4 gram of *p*-toluidine to the benzene.

The experiment may be repeated to determine the molecular weight of nitrobenzene, quantities of 0·25, 0·25 and 0·5 gram being added.

(ii) *Determine the Degree of Association of Benzoic Acid in Benzene Solution.* Add quantities of 0·1, 0·2, 0·2, 0·5 and 1·0 gram of benzoic acid. Calculate the degree of association, assuming that two simple molecules of benzoic acid associate to form one complex molecule. Find the influence of concentration on the association, by plotting the degree of association against the concentration of the solution.

(iii) *Determine the Degree of Dissociation of Potassium Chloride in Water Solution.* An intimate mixture of powdered ice with a little salt should be used as the freezing mixture for this experiment. Add quantities of potassium chloride of 0·1, 0·1, 0·2, 0·2, 0·5 and 0·5 gram. The degree of dissociation should be expressed along with the concentration. A curve may also be drawn showing the influence of concentration on the degree of dissociation.

2. Solvents which are Solid at Ordinary Temperature

The use of melted solid substances as solvents, in the determination of molecular weight, involves exactly the same principle as the use of liquid solvents, but since these solvents have usually a very large "Depression Constant," it is unnecessary to use a Beckmann thermometer, and consequently a thermometer reading to $\frac{1}{10}$ degree may be substituted for it.

The apparatus necessary, consists of a test tube A (Fig. 40), supported by a cork in the neck of a somewhat wider tube B, which serves as an air jacket. The tube A is fitted with a cork which carries a thermometer T and a stirrer S, made of stout platinum wire. The two tubes are supported in a beaker of water or other liquid, which can be raised to the required temperature by a carefully regulated flame. The method of carrying out the experiment is the same as that already described.

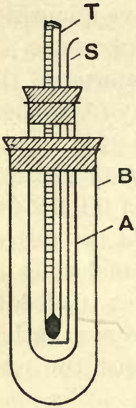

FIG. 40.

EXPERIMENT

Determine the Molecular Weight of a-Naphthol in Azobenzene Solution. Use about 10 grams of azobenzene as solvent for this experiment. Melt it in a water bath at about 73°–74°. When all is melted remove the flame and allow the water to cool slowly, keeping both the water and azobenzene well stirred until solidification takes place. Under no circumstances should the temperature of the water bath be more than one degree below the freezing point of the azobenzene when the freezing point is read. Three readings of the freezing point should be made and the mean value taken. Then add about 0·15 gram of α-naphthol, and again melt the whole; stir well to ensure complete solution, and cool as before, noting the temperature of solidification. Repeat, adding further quantities of 0·1 and 0·2 gram of α-naphthol.

CHAPTER VIII

SOLUBILITY DETERMINATION

THE solubility is a factor which enters frequently into the calculations of many physico-chemical determinations, hence a short description of the methods adopted for its determination is necessary here. Solubility determinations for the present purpose can be considered under three heads: (i) solubility of gases in liquids, (ii) solubility of liquids in liquids, and (iii) solubility of solids in liquids.

By the solubility of a substance in a liquid, one understands, in the case of solids, the weight of the solid dissolved by a given weight of the solvent, generally 100 grams, to form a saturated solution at a given temperature. The solubility of liquids and gases is generally expressed as the volume dissolved by a given volume of the solvent to form a saturated solution at a given temperature. As in all cases, the solubility varies with the temperature, this must always be stated along with the solubility.

1. Solubility of Gases in Liquids

a. **Sparingly Soluble Gases.** For the determination of the solubility of those gases which are not excessively soluble in the liquid in question, the apparatus due to Ostwald may be employed. This consists of a gas burette A (Fig. 41), of about 150 c.c. capacity, connected to a levelling tube L. The burette is connected to an absorption vessel B, of about 75 c.c. capacity, which is fitted with a three-way tap *t* and a two-way tap *s*. All connections between the two pieces of the apparatus are made by short pieces of stout-walled rubber tubing, which are wired on. Before making an experiment, the volume of the absorption vessel between the taps *s* and *t* must be determined. This can be done most easily by filling it with mercury, and running the mercury into a graduated measuring vessel. In making an experiment, the absorption vessel is filled with the solvent, and both taps *s* and *t* are closed. Then the upper tube of the tap *s* is carefully dried on the inside by means of filter paper.

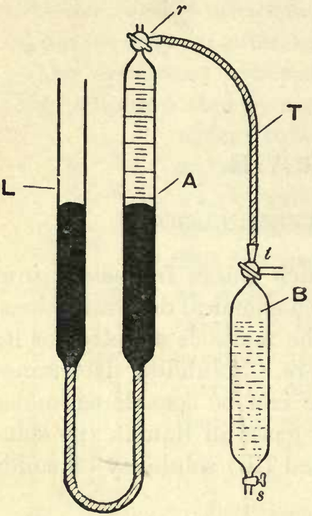

Fig. 41.

The burette is then connected with the absorption vessel, as indicated in the diagram, and the tap *r* is turned so that the burette is open to the air. The levelling tube is raised until the burette and tap are full of mercury. The burette is then connected to a gasholder containing the gas whose solubility is to be determined, and the gas is admitted into A by lowering L. When sufficient gas has been taken into F, the taps *r* and *t* are turned, so that the gas from the holder may flow through the connecting tube T, and so fill it. The tap t is then closed, and r is turned so that the burette and connecting tube are in communication, and the apparatus allowed to stand for about 20 minutes until the contents have taken on the surrounding temperature. The levelling tube is then adjusted, and the volume of the gas read. A graduated measuring vessel is then placed under s, which is opened, and then the burette and absorption vessel are placed in communication with one another by opening t. A quantity of the solvent, about 30 c.c., is expelled from B by raising the levelling tube L, and then the tap s is closed. The liquid driven out is carefully measured, and the absorption vessel gently shaken until the height of the mercury in A remains stationary, when the volume of the gas is again read.

Care must be exercised in shaking B that none of the liquid is thrown into the tap. Should the solubility be required at a given temperature, the absorption vessel must be immersed in a thermostat at that temperature. If t is the temperature of the absorption vessel, B the barometric pressure, v_1 the initial reading of the burette and v_2 the final reading, t_1 the temperature of the burette, v_0 the volume of liquid expelled from the absorption vessel, v the volume of the absorption vessel and p the vapour tension of the liquid at the temperature of the experiment, then if s is the solubility,

$$s = \frac{(v_1 - v_2)\frac{\mathrm{B}}{\mathrm{B} - p}\left(\frac{1 + at_1}{1 + at}\right) - v_0}{v - v_0} \text{ c.c.'s per c.c.}$$

EXPERIMENT

Determine the Solubility of Carbon Dioxide in Water at room temperature. In this experiment, admit about

120 c.c. of carbon dioxide into the burette, and leave from 30–40 c.c. of water in the absorption vessel. The water used for this experiment must be freshly boiled distilled water, which has been allowed to cool out of contact with air.

b. **Very Soluble Gases.** The solubility of gases which are extremely soluble in liquids, *e.g.* ammonia or hydrochloric acid in water, cannot be determined by the method described above. To determine the solubility of such gases, a thin-walled glass vessel of the shape indicated in Fig. 42 is used; this vessel should have a capacity of about 30 c.c. It is carefully cleaned, dried and weighed; a small quantity of the solvent, about 10–15 c.c., is then drawn into it, and the whole again weighed. The vessel is then placed in a thermostat, and a current of the gas in question passed into it until no more is absorbed. The vessel is then sealed at both ends and re-weighed. This gives the weight of the solution, and if it were permissible to assume that none of the solvent had been lost during the experiment, by being carried away by the stream of gas, the solubility could be directly calculated. This, however, may not be done, and to obtain an accurate result from the experiment, it is necessary to adopt some chemical method for determining exactly the quantity of gas in the measured weight of solution. General directions cannot be given to meet all cases, but if the solubility of ammonia or hydrochloric acid were in question, the bulb could be broken under a measured volume of normal sulphuric acid or soda respectively, and the excess of the normal solution obtained by titration.

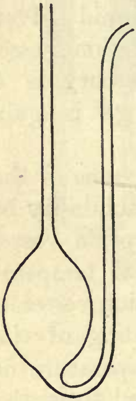

FIG. 42.

This would then give the weight of the gas in a given weight of solution, from which the amount in a given weight of the solvent could be obtained. A correction ought to be applied for the amount of gas contained in the bulb above the saturated solution, which has been weighed and estimated along with that in solution.

EXPERIMENT

Determine the Solubility of Sulphur Dioxide in Water at 25°. Carry out this experiment exactly as described above. The gas may be conveniently obtained from a syphon of liquid sulphur dioxide. To estimate the amount of gas absorbed, break the vessel, after weighing, in a beaker containing 250 c.c. of standard potassium permanganate solution, which has about 5 grams potassium permanganate to the litre. The excess of potassium permanganate may then be titrated with $\frac{N}{5}$ oxalic acid solution. In breaking the bulb, the best method is to scratch a file mark on both tubes near the bulb, then hold the bulb under the permanganate, and break off the tubes by pressing them against the side of the beaker with a glass rod. The bulb must then be crushed by tapping it with a glass rod. If the bulb is not entirely covered by the permanganate solution, a quantity of freshly boiled and cooled water may be added, to completely cover it. Compare the solubility obtained with that calculated from the weighings alone.

2. Solubility of Liquids in Liquids

Liquid pairs fall into two groups with respect to their mutual solubility: (i) those pairs of liquids which are soluble in one another in all proportions, and (ii) those pairs which are soluble to a definite extent in one another. The solubility in the first case is an unlimited quantity and does not concern us here; in the second case, however, it is a perfectly definite quantity, and can be determined in the following manner:

The two liquids, in approximately equal quantities, are placed in a 250 c.c. stoppered bottle; the stopper and neck of the bottle are covered by an indiarubber cap, which is tied tightly on to the neck, so that the stopper is held firmly in its place and nothing may enter the bottle. The bottle is then placed in a thermostat and shaken for 2–3 hours, then it is removed from the shaker, and allowed to stand in the bath until its contents have settled into two layers. If at this point it is noticed that only one layer has formed, more of one of the liquids must be added, and the shaking repeated. When the two layers have separated and are quite clear, a measured quantity of the top layer, *e.g.* 10 c.c., is pipetted off and analysed. The bottle is then closed again and shaken for one hour longer, and the top layer analysed; if both analyses agree, then it may be taken that the solutions are saturated. Should the analyses not agree, the bottle must be shaken again, until two successive analyses agree. When the saturation point has been reached, a quantity of the bottom layer may also be removed and analysed. This is done by closing the top of the pipette with the finger, and inserting it below the top layer and then filling in the usual way; on removing the pipette, the outside should be carefully wiped, to prevent any liquid which may be adhering to the outside from running down and mixing with the contents of the pipette as they are run out for the purpose of analysis. No general directions can be given for the analysis of the various liquid solutions; the method of treatment must be devised to suit the substances under consideration. Occasionally it happens that the boiling points of the two liquids are far apart; when this is the case, the more volatile may be distilled off from a known weight of the mixture, and the residue weighed. The result will be much more accurate, however, if some purely chemical method of analysis can be employed, *e.g* titration.

Experiment

Determine the Solubility of Aniline in Water at 25°. In this experiment use about 20 c.c. of aniline and 100 c.c. of water, and saturate them with one another as described above; after shaking, analyse the aqueous solution, *i.e.* the top layer. The quantity of aniline present in this, may be determined by titrating the solution with a standard solution of potassium bromide and potassium bromate, in the presence of hydrochloric acid. The standard solution, which must contain the bromide and bromate in the proportion of 5 molecules of the former to 1 molecule of the latter, is best made up by cautiously adding bromine to a saturated solution of caustic potash, until no more is taken up. The solution is then diluted to dissolve any crystals which may have formed, and more bromine is added and finally bromine water, until the solution has only a faint alkaline reaction. The solution now contains bromide and bromate in the required proportion. It has now to be standardised, by titrating weighed quantities of aniline with it, and brought to such a strength that about 20 c.c. of it are equivalent to 0·5 gram of aniline. The titration is effected in the following manner: about 0·5 gram of aniline is diluted with 20 c.c. of water, and 10 c.c. of concentrated HCl are added, and the standard solution added slowly in small quantities. The flask in which the titration is being carried out must be vigorously shaken after each addition, a white precipitate of tribromaniline is formed and a clear colourless solution left. The end of the reaction is indicated by the solution becoming faintly yellow. The following equations represent the course of the reaction:

$$KBrO_3 + 5KBr + 6HCl = HBrO_3 + 5HBr + 6KCl$$
$$HBrO_3 + 5HBr = 3Br_2 + 3H_2O$$
$$C_6H_5NH_2 + 3Br_2 = C_6H_2Br_3NH_2 + 3HBr.$$

Take 20 c.c. of the saturated solution for each titration and add 20 c.c. of water and 10 c.c. of concentrated hydrochloric acid.

3. Solubility of Solids in Liquids

To determine the solubility of a solid in a liquid, a quantity of solid, sufficient to saturate the liquid, is finely powdered and placed in a stout bottle fitted with a well ground stopper. A quantity of the solvent is added, the bottle closed, and the neck and stopper covered by a rubber cap. The bottle is then placed in a thermostat and shaken for 3–4 hours. The bottle is then removed from the shaker and allowed to stand in the thermostat until its contents have settled. When the solution is perfectly clear, a measured quantity is removed by means of a pipette and analysed. The bottle is then shaken for 2 hours and the solution analysed again. Shaking must be persisted in until two successive shakings do not change the concentration of the solution. The method of obtaining a saturated solution may be varied in the following manner: the solvent containing an excess of the solid is heated to a temperature considerably above that at which the solubility is to be determined.

The solution, in this way, already contains more of the solid than it can hold at the experimental temperature. It is then placed in a bottle, together with a small quantity of the solid, and shaken at the required temperature in a thermostat, as described above, until the analysis of the solution gives constant results.

This method of producing a saturated solution is apt to lead to results which are too high, whilst the first method may give results which are too low. The best method of procedure is to start the saturation from both sides, *i.e.* from a supersaturated solution, and from the pure solvent, and shake until both give the same result.

It is generally found in solubility determinations that the more soluble the substance, the more quickly it reaches saturation, but no general rule can be stated to furnish a guide as to the length of time required for saturation. The majority of the salts, which are generally known as easily soluble salts, reach saturation in from 3–4 hours, whilst the so-called "insoluble" substances often require to be shaken for days and even weeks before saturation is attained.

The removal of the saturated solution is effected by a dry pipette, calibrated to withdraw a definite volume, if the solubility is required in terms of the weight of dissolved substance in a measured volume of solution. The pipette is emptied into a beaker in the usual way, and thoroughly washed out with distilled water, the washings being added to the saturated solution in the beaker. If the solubility is required in terms of the weight of dissolved substance in a given weight of water, the solution may be withdrawn by any dry pipette, and transferred to a tared weighing bottle, and then weighed. Should the temperature at which saturation has been effected be much above the atmospheric temperature, the pipettes used for withdrawal must be warmed before being used to extract the liquid, to prevent deposition of the solid taking place in them.

The method of analysis to be adopted depends, as in the case of liquids, upon the nature of the dissolved substance. Solids which are quite stable at temperatures 10°–20° above the boiling point of the solvent, may be determined by driving off the solvent by evaporation, and then heating the residue to a temperature a few degrees above the boiling point of the solvent for 15–20 minutes, weighing and re-heating until the weight is constant. Substances which are not stable toward heat must be determined by the usual analytical methods, either volumetric or gravimetric. In this connection it must always be remembered that, frequently, these saturated solutions are much too concentrated to be analysed directly, and they must therefore be diluted to a known volume, and an aliquot part taken for analysis. Those solids which, by reason of their small solubility, *e.g.* silver chloride, barium sulphate, etc., cannot be determined by the foregoing methods, are determined by the methods of electro-chemistry. (See chapters on Electro-conductivity, and Electromotive force, Part II.)

EXPERIMENTS

(i) *Determine the Solubility of Potassium Chloride in Water at* 25°. Place about 40 grams of powdered potassium chloride, and 100 c.c. of distilled water in a stoppered bottle; in a second bottle place a little solid potassium chloride and about 100 c.c. of potassium chloride solution, which has been prepared by boiling water with an excess of potassium chloride for a few minutes. Shake both for 3–4 hours, allow the contents to settle and then transfer 10 c.c. of each to weighed platinum dishes, and remove the water by heating on a water bath. Dry the solid at 120° for 15 minutes, and weigh. Shake the bottle for 1 hour longer and re-determine, if both the former results do not agree. Express the result in grams of potassium chloride per 100 grams of water, and also per 100 c.c. of solution.

(ii) *Determine the Solubility of Ammonium Chloride in Water at* 25°. Use 45 grams of ammonium chloride and 100 c.c. of water for this experiment. Shake for 3–4 hours, and after the solution has settled, withdraw and weigh about 10 grams of the solution, transfer it to a litre measuring flask and fill up to the mark. Titrate 25 c.c. of the diluted solution with $\frac{N}{10}$ silver nitrate solution. Express the result in grams per 100 grams of water.

(iii) *Determine the Solubility of Potassium Iodide in Ethyl Alcohol at temperatures from* 10°–30°. Place about 15 grams of powdered potassium iodide and 100 c.c. of absolute alcohol in a stoppered bottle; allow the bottle and contents to stand in the thermostat for 15 minutes before inserting the stopper. This is to avoid pressure, owing to the vapour pressure of the alcohol. Then stopper the bottle and shake at a constant temperature for 5–6 hours. The analysis in this case may be effected by evaporating the alcohol on a water bath and drying the residue in a steam oven for 15–20 minutes.

Plot the solubilities obtained against the temperatures, and so obtain a solubility curve of potassium iodide in alcohol.

CHAPTER IX

VISCOSITY AND SURFACE TENSION

1. Viscosity

WHEN a liquid flows through a tube its molecules do not move freely past one another, but are retarded by a frictional force termed viscosity. If a volume v of a liquid, driven by a pressure p, flows through a tube of length l and radius r in a time t, then

$$v=\frac{\pi r^4 pt}{8l\eta}, \quad i.e. \quad \eta=\frac{\pi r^4 pt}{8lv},$$

where η is the coefficient of viscosity. This expression is derived on the assumption that the molecules of a liquid move in straight lines parallel to the axis of the tube, and that the layer of molecules contiguous to the walls of the tube are motionless, whilst those in the centre have the greatest velocity. The coefficient of viscosity may be defined as the force necessary to move unit area of a liquid through unit distance over an adjacent layer of the same liquid situated unit distance away. The coefficient of viscosity determined by means of the above formula, where the various factors are measured in C.G.S. units, is naturally obtained in absolute units. The absolute determination of η is often a tedious process and liable to many errors, so for this reason it is usual, for physico-chemical purposes, to determine the "relative" or specific viscosity of a liquid, using some well defined substance, generally water at 25°, as the standard, and comparing other liquids with it.

In calculating the coefficient of viscosity from the above formula, a necessary condition is that the pressure p shall be just sufficient to drive the liquid through the tube, *i.e.* the liquid shall have zero velocity as it leaves the tube. Naturally this condition cannot be fulfilled, hence a correction, representing the kinetic energy of the liquid as it leaves the tube, has to be introduced into the equation, the corrected expression reading

$$\eta = \frac{\pi r^4 pt}{8lv} - \frac{vd}{8\pi tl},$$

where d is the density of the liquid.

Experimentally, the conditions are so chosen that the correction factor becomes so small that it may be neglected. That this may be so, it is customary to use long narrow capillary tubes for the determination, and small pressures.

The apparatus generally adopted for the determination of the coefficient of viscosity is the Pouseuille apparatus as modified by Ostwald. It consists of a fine capillary tube ab (Fig. 43) about 0·25–0·4 mm. diameter and 10–12 cm. long, this is fused at its upper end to a wider tube B, which is blown into a small bulb D close to the capillary tube. The bulb is of such dimensions that its contents would require at least 100 seconds to flow through the capillary tube.

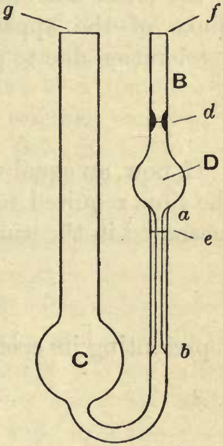

FIG. 43.

The lower end of the capillary tube is also fused to a wider tube, which is bent and provided with a bulb C, as indicated in the diagram. Two marks *d* and *e* are etched on the tube just above and below the bulb D. It is essential that the space between the bulb D and the capillary shall be perfectly smooth and regular, and that the tube and joint at the top of the bulb D shall be wide enough to prevent drops of liquid hanging.

To carry out a determination, a known volume of liquid is introduced into C by means of a pipette, this is then drawn into the bulb D so that the upper level of the liquid is above the mark *d*, by sucking at *f* or blowing into the apparatus at *g*. The time required for the upper meniscus of the liquid to pass from the mark *d* to the mark *e* is then noted by means of a stop-watch. The liquid is driven through the capillary by its own pressure, which is equal to $h.d.g$, where h is the mean difference of height of the liquid in the two limbs of the apparatus, d is the density and g the acceleration due to gravity, hence

$$\eta = \frac{\pi r^4 thgd}{8vl}.$$

If, now, an equal volume of another liquid be taken, and the time required for it to flow through the capillary be measured in the same way, we shall have the expression

$$\eta_1 = \frac{\pi r^4 t_1 h d_1 g}{8vl},$$

representing its coefficient of viscosity; or

$$\frac{\eta}{\eta_1} = \frac{dt}{d_1 t_1},$$

i.e. the coefficients of viscosity of the two liquids bear the same relation to one another as the products of their densities and the times of their outflow. If, now, η be taken as the value of the standard liquid, then the relative viscosity of the second liquid is known. The absolute viscosity may be obtained by inserting the value of the absolute viscosity of the standard liquid in the above equation. The absolute viscosity of water at 25° is $8{\cdot}91 \times 10^{-3}$, hence

$$\eta_1 = \frac{d_1 t_1}{dt} \times 8{\cdot}91 \times 10^{-3}.$$

The coefficient of viscosity varies considerably with temperature, about 2 per cent. per degree, hence all determinations should be carried out in a thermostat. For the methods of determining absolute viscosity, the reader is referred to the original paper of Thorpe and Rodger (*Phil. Trans.* 185A, 397).

EXPERIMENTS

(i) *Determine the Specific Viscosity of Alcohol at* 25°. Fit up a large beaker, 2–3 litres capacity, as a water thermostat, and arrange it by means of a temperature regulator, so that the temperature remains constant at 25°. Clean and dry the viscosity tube, and fix it in the thermostat so that the upper mark is below the surface of the water. Then add 10 c.c. of boiled and cooled distilled water, and allow to stand for 20 minutes, so that the tube and contents may acquire the temperature of the bath. Attach a piece of indiarubber tubing to the narrower tube of the apparatus, and suck up the liquid until the upper meniscus stands 2–3 cm. above the higher graduation mark *d*. Now allow the water to flow back through the capillary tube into the lower bulb, and measure the time required for the meniscus to pass from *d* to *e*, by starting a stop-watch as it passes *d* and stopping it when *e* is reached. Repeat the measurement several times, and take the mean of the determinations as the value. The separate determinations should not differ by more than 0·2 per cent. from the mean value. If a greater variation is found in the determinations, the capillary tube is either greasy or choked by dust particles, which must be removed before the experiment can be carried out. The apparatus must now be emptied and dried, and 10 c.c. of pure ethyl alcohol added. Place the apparatus back in the thermostat, and, proceeding exactly as before, determine the time of outflow of the alcohol.

From the formula

$$\eta_1 = \eta_0 \frac{d_1 t_1}{d_0 t_0}$$

calculate the specific viscosity of the alcohol, taking the value of water as unity. The density of water at 25° $=0·997$ and that of absolute alcohol $=0·785$. Further, from the value of the absolute viscosity of water, $8·91 \times 10^{-3}$, calculate the absolute viscosity of alcohol.

(ii) *Determine the Change in Viscosity by substituting various groups for Hydrogen.* This experiment is carried out exactly as the last. First determine time of outflow of water and then of the other substances. A good series of substances for this experiment is, benzene, chlorbenzene, brombenzene, iodobenzene, aniline and nitrobenzene. The various substances must be quite pure and freshly distilled before being used for the experiment. Information on the constitutive influence of the various groups on the viscosity may be found in the paper by Thorpe and Rodger referred to above.

2. Surface Tension

The molecules at the surface of a liquid are in a different condition from the molecules in any other portion of the liquid, for those situated in the interior of a liquid are subjected, on all sides, to the attractions of the other molecules, whereas those at the surface are only subjected to these attractions on the side which is immersed in the liquid, the half directed outward not being in the liquid, is free from these attractions. Hence a molecule at the surface of a liquid is subjected to a series of forces, the resultant of which acts at right angles to the surface, and tends to draw the molecule in question into the interior of the liquid. This force acting toward the interior of the liquid is termed the "surface tension." It tends to make the surface of a liquid as small as possible, and gives rise to the phenomena of capillarity. The surface tension is defined as the force which acts at right angles to the surface of a liquid, along a line of unit length; it is generally represented by the symbol γ.

There are several methods of determining the surface tension of liquids, two of which are made use of for physico-chemical purposes, viz. the measurement of the rise of liquids in capillary tubes, and the determination of the weight of falling drops of liquids.

When a capillary tube is dipped into a liquid, the liquid will rise in the tube to such a height that the weight of the column of liquid exactly counterbalances the surface tension of the liquid. If we assume that the liquid makes an angle θ with the walls of the tube, then,

$$\gamma \cos \theta \, . \, 2\pi r = \pi r^2 h d,$$

where h is the height of the column of liquid in the capillary tube, d its destiny, and r the radius of the tube.

If it be assumed that the liquid wets the walls of the tube, then the value of θ becomes equal to zero, and

$$\gamma = \tfrac{1}{2}hrd.$$

This expression does not take account of the weight of the liquid forming the meniscus; this may be taken into the calculation by increasing h by one-third of the radius; the expression then becomes

$$\gamma = \tfrac{1}{2}rd\left(h + \frac{r}{3}\right).$$

In addition to γ another constant is often employed for physico-chemical purposes, termed the specific cohesion, this is symbolised by a^2, and has the value

$$a^2 = \frac{2\gamma}{d}.$$

Since $\gamma = \tfrac{1}{2}hrd$, it will be seen that the specific cohesion is measured by the height to which a liquid will rise in a tube of unit radius.

If a liquid be allowed to flow through a long narrow tube, it will form a drop at the open end, which will slowly increase in size to a maximum, and then fall off. The drop falls when its weight just exceeds the surface tension.

If W represents the weight of the drop just before it falls, then

$$\gamma = \frac{\mathsf{W}}{2\pi r}.$$

If a liquid be withdrawn from the action of gravity by placing it in another liquid of the same density, with which it does not mix or react, it will assume a spherical form. The surface area of the sphere taken up by one gram molecule of a liquid under such conditions is known as the "molecular surface" of the liquid. If it be assumed that the molecular volume of the liquid is V, then the molecular surface may be expressed by $\mathsf{V}^{\frac{2}{3}}$. If this now be multiplied by the surface tension, an expression $\gamma\mathsf{V}^{\frac{2}{3}}$ is obtained which is known as the "molecular surface energy." This quantity is generally expressed $(\mathsf{M}v)^{\frac{2}{3}}\gamma$, where M is the molecular weight and v the specific volume of the liquid. The molecular surface energy decreases regularly with increase of temperature, and the temperature coefficient is the same for all non-associated liquids, namely, 2·12. This value is obviously equal to the difference of the molecular surface energy at two different temperatures, divided by the difference of the temperatures:

$$\frac{\gamma_0(\mathsf{M}v_0)^{\frac{2}{3}}-\gamma_1(\mathsf{M}v_1)^{\frac{2}{3}}}{t_1-t_0}=2{\cdot}12,$$

and furnishes a method for the determination of the molecular weight of non-associated liquid or molten substances.

In many cases, however, the coefficient obtained is smaller than 2·12, and a much larger molecular weight must be attributed to the liquid in order to obtain the value 2·12. If in such a case x represents the factor by which the molecular weight must be multiplied to give the value 2·12, then

$$\frac{\gamma_0(x\mathsf{M}v_0)^{\frac{2}{3}}-\gamma_1(x\mathsf{M}v_1)^{\frac{2}{3}}}{t_1-t_0}=2{\cdot}12,$$

whereas $$\frac{\gamma_0(\mathsf{M}v_0)^{\frac{2}{3}}-\gamma_1(\mathsf{M}v_1)^{\frac{2}{3}}}{t_1-t_0}=\mathsf{K}.$$

Dividing these two expressions we get

$$x=\left(\frac{2{\cdot}12}{\mathsf{K}}\right)^{\frac{3}{2}},$$

where x represents the mean association factor of the liquid over the temperature range $t_0 - t_1$, *i.e.* the number by which the molecular weight, representing the unassociated molecule, must be multiplied to give the mean molecular weight of the liquid.

1. Method of Capillary Rise. The apparatus required for this method consists of a stout-walled capillary tube A (Fig. 44), 0·2–0·3 mm. diameter bore, and about 15–20 cm. long; this is fastened by two pieces of platinum wire to an opal glass scale B which is graduated in millimetres. The whole is then placed in a tube C slightly wider than the scale. The capillary must be quite vertical; this is best achieved by having the capillary somewhat longer than C, and passing through a cork which closes the tube C; a second hole should be bored in the cork so that atmospheric pressure prevails in the tube. Before attaching the capillary to the scale, it must be thoroughly cleaned by drawing a hot chromic acid mixture through it, for some minutes, by means of a pump. Then it must be washed with distilled water in the same way, and finally dried by drawing a stream of filtered air through it. On no account must a tube, which is to be used for surface tension determinations, be washed with alcohol or ether, for these substances generally leave the tube greasy. Care must also be taken not to handle the tube near the ends, or grease will be left on from the fingers, and this coming

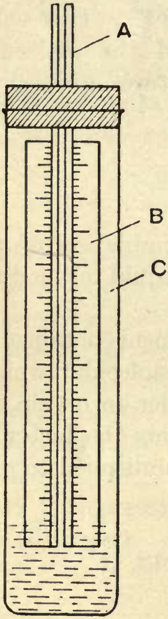

Fig. 44.

in contact with the liquid will change its surface tension.

Before commencing a determination of surface tension, the bore of the capillary must be examined to see that it is uniform, and then its radius must be determined. The former operation is best carried out by introducing into the capillary attached to the scale a drop of mercury which will fill from 3–5 mm. of the tube. This is moved from place to place along the tube, and its length measured on the scale in the various places. If it should have markedly different lengths the tube must be rejected. Having obtained a tube of uniform bore, its radius may then be determined.

The most suitable method is to fill the tube with mercury, and then expel the mercury into a tared weighing bottle, and weigh it. If l is the length of the tube in millimetres, w the weight of the mercury in milligrams, t the temperature and r the radius of the tube, then

$$r=\sqrt{\frac{w(1+0{\cdot}000181t)}{13{\cdot}596\pi l}},$$

where 0·000181 is the mean coefficient of cubical expansion of mercury, and 13·596 is its density. Three determinations of the radius should be made and the mean value used. The radius may also be obtained by taking a liquid of known surface tension, and, from the height it rises in the tube, calculating the radius by means of the formula

$$\gamma=\tfrac{1}{2}hrdg.$$

EXPERIMENTS

Determine the Surface Tension of Benzene at 25°. Having cleaned a capillary tube, examine its bore and determine its radius as indicated above. Then place about 5 c.c. of benzene into the wide tube C (Fig. 44) and place it in a thermostat at 25°. A large beaker may be used for this purpose. Place the capillary and scale in the tube and allow the apparatus to stand in the thermostat for 20 minutes, *i.e.* until it has acquired the temperature of the bath. Then attach a clean piece of rubber tubing to the projecting end of the capillary tube, and draw the benzene up and down the tube several times, by alternately sucking and blowing, until the walls of the capillary are thoroughly wetted. It is well to attach a glass mouth-piece to the rubber tube, which should be filled with cotton wool, to prevent moisture and grease reaching the capillary. Care must also be taken that the benzene is not drawn into the rubber tube. Now allow the benzene to rise in the capillary until it has come to its equilibrium point, then read the level of the benzene in the tube, and also at the bottom outside the tube, by means of a lens. Repeat the experiment three or four times, blowing the liquid out of the tube each time. A variation may be made by drawing the liquid higher up the tube than its equilibrium point and allowing it to fall to the correct position. If the readings differ by more than 0·3 mm. the capillary is dirty and must be cleaned, and the measurements repeated. Calculate the result by the formula

$$\gamma = \tfrac{1}{2} hrdg.$$

The density of benzene at 25° is 0·872.

(ii) *Determine the Association Factor for Water.* In this experiment the surface tension must be determined at two different temperatures, which are best chosen lying about 20° apart. Calculate the association factor from the values obtained, by using the formulae

$$K=\frac{\gamma_1(Mv_1)^{\frac{2}{3}}-\gamma_2(Mv_2)^{\frac{2}{3}}}{t_2-t_1}$$

and $$x=\left(\frac{2\cdot12}{K}\right)^{\frac{3}{2}}.$$

The values for v_1 and v_2 are obtained from the densities (Table II. Appendix): $v_1=\frac{1}{d_1}$ and $v_2=\frac{1}{d_2}$, where d_1 and d_2 are the densities of water at t_1° and t_2° respectively.

2. **Method of Falling Drops.** The apparatus for the determination of the surface tension by this method is made up of two parts: (i) the dropping tube, and (ii) the pressure apparatus. The former consists of a tube A (Fig. 45), bent twice at right angles as in the diagram; the vertical part of the tube *bc* is 2–3 mm. diameter, and has a bulb B blown in it of 6–8 c.c. capacity. This tube is

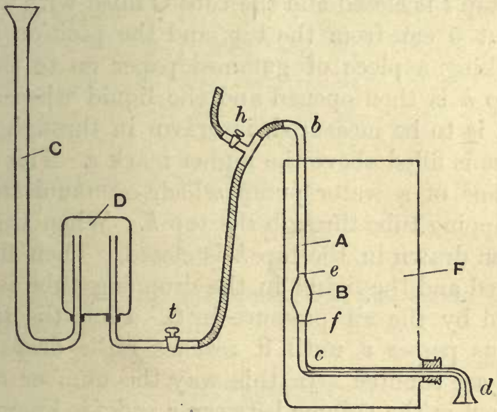

FIG. 45.

carefully joined to a capillary tube, 0·2–0·3 mm. diameter, which forms the lower portion *cd* of the dropping tube. The end *d* is carefully pressed out so that it has a conical shape, and then it is ground perfectly flat. Two marks, *e*, *f*, are etched on the tube, one just above and the other just below the bulb B. The dropping tube is supported in a vessel F, which can be kept at constant temperature. The pressure apparatus consists of a long glass tube C, about 100 cm. long and 2 cm. diameter, which is connected to a large inverted Woullf's bottle D of about 1 litre capacity, as illustrated in the diagram. The second tubulus of the bottle is connected directly with the dropping tube. By filling C with water, a constant air pressure can be set up, which may be communicated to the dropping apparatus.

The determination is carried out in the following manner:

The tap *t* is closed and the tube C filled with water up to about 5 cm. from the top, and the position marked by sticking a piece of gummed paper on to the tube. The tap *h* is then opened and the liquid whose surface tension is to be measured, is drawn in through *d* until the tube is filled above the higher mark *e*. This is done by means of a water pump which communicates with the dropping tube through the tap *h*. When the liquid has been drawn in, the tap *h* is closed. Then the tap *t* is opened and the liquid in the dropping tube is slowly expelled by the air pressure in D. From the time the meniscus passes *e* until it reaches *f* the drops falling from *d* are counted. In this way the number of drops contained in the volume between *e* and *f* is known. The pressure must be so adjusted that the liquid drops at the rate of not more than one drop in 5–6 seconds. The pressure must also be kept constant during the experiment; this is secured by keeping the height of the column of water in C constant, which can best be done by placing a tap funnel above it so regulated that it delivers water at the same rate as the water flows from C. It is important that the temperature be kept constant during the experiment. It is usual to determine, first the number of drops of water contained in the measured volume, and then the number contained in the same volume of the liquid whose surface tension is to be measured. If n_1 and n_2 represent the number of drops of water and the other liquid, respectively, contained in the measured volume, and a_1^2 and a_2^2 their specific cohesions, and if θ_1 and θ_2 represent the angles which these liquids, respectively, make with the walls of the tube, then

$$a_1^2 \cos \theta_1 = \frac{a_2^2 \cos \theta_2 n_2}{n_1}.$$

Since $\gamma_1 \cos \theta_1 = \frac{1}{2} hrd_1$ and assuming that $\cos \theta_1 = 1$ for water, we have

$$\frac{2\gamma_2 \cos \theta_2}{d_2} = \frac{2\gamma_1}{d_1} \cdot \frac{n_1}{n_2},$$

or,

$$\gamma_2 \cos \theta_2 = \gamma_1 \frac{n_1}{n_2} \cdot \frac{d_2}{d_1}.$$

If the angle θ_2 is zero, then

$$\gamma_2 = \gamma_1 \frac{n_1}{n_2} \cdot \frac{d_2}{d_1}.$$

If the value of θ_2 is unknown, then the factor $\gamma \cos \theta$ is all that can be determined by this method.

EXPERIMENT

Determine the Surface Tension of Alcohol at 25°. Carry out the experiment exactly as described. Clean the dropping tube, before using it, with chromic acid mixture, and make three or four determinations, first with water and then with alcohol. Freshly distilled alcohol must be used, and care must be taken that it does not come in contact with any greasy substance. The flasks or vessels in which it is contained should be cleaned with chromic acid mixture before it comes in contact with them. It may be assumed in the calculation, that the alcohol and water both completely wet the tube, *i.e.* in both cases $\cos\theta = 1$. The density and surface tension of water will be found in Tables II. and VI. Appendix, respectively, the density of absolute alcohol at 25° = 0·785.

CHAPTER X

POLARIMETRY

Many organic liquids and solutions of organic solids, have the property possessed by quartz crystals and other mineral substances of rotating the plane of polarised light. These substances are said to be optically active. Whether a substance is optically active or not, may be determined by examining it between a pair of Nicol prisms.

When a beam of light is passed through a Nicol prism, it emerges with all its vibrations taking place in one plane; it is then said to be plane polarised. Should this polarised beam be allowed to enter a second Nicol prism, it will be found that on rotating the second prism, the light will be allowed to pass through and be completely stopped alternately, twice during the complete revolution of the prism, *i.e.* the field observed in the second Nicol prism will be alternately dark and light, the maximum and minimum brightness occurring at positions 90° apart. If two Nicol prisms be placed with their axes at right angles, *i.e.* so that the field observed in the second prism is dark, and a tube containing an optically active liquid be placed between them, the field will become light, due to the rotation of the polarised beam by the optically active substance. The amount through which the plane of the polarised beam has been rotated can be determined by measuring the angle through which the second Nicol prism must be rotated to make the field dark again. When the prism has to be rotated to the right, *i.e.* clockwise, to produce a dark field, the substance is said to be "dextro-rotatory," and when it has to be rotated to the left, the substance is termed "laevo-rotatory." From what has been already said, it will be obvious that a position of darkness could be regained by rotating the prism in either direction, since there are two positions of darkness 180° apart. It is customary to choose the direction where the angle through which the prism must be turned is less than 90°.

The angle of rotation, *i.e.* the angle through which the plane of polarised light is rotated, is dependent on the nature of the substance, the length of the column of the substance through which the light has to pass, the temperature at which the observation is made, and the wave length of the light used in the determination. The last factor makes it necessary to employ monochromatic light for all polarimetric determinations.

The results of polarimetric determinations are expressed either as the specific rotation, or the molecular rotation, and in stating these quantities the temperature of observation and the wave length of the light used must always be specified.

The specific rotation is obtained by dividing the angle through which a column of the substance rotates the plane of polarised light, by the product of the length of the column and the density.

$$[a]=\frac{a}{ld},$$

where $[a]$ is the specific rotation or the specific rotatory power, a is the observed angle, l the length of the column of liquid in decimetres and d the density of the liquid. If this value be multiplied by the molecular weight of the substance, the molecular rotation is obtained, but as the numbers obtained in this way are so large, it is usual to call one-hundredth of this value the molecular rotation, thus

$$[m] = \frac{ma}{100ld},$$

where m is the molecular weight and $[m]$ the molecular rotation.

The measurement of $[a]$ and $[m]$ may also be carried out with solutions of optically active substances, if the assumption be made that the solvent has no action on the plane of polarised light. This assumption is generally not permissible, but may be made in the case of aqueous solutions.

If w grams of an optically active substance be dissolved in v c.c. of the solvent, then

$$[a] = \frac{av}{lw} \quad \text{and} \quad [m] = \frac{m}{100} \cdot \frac{av}{lw};$$

or, if the composition of the solution is known by weight, so that w grams of the active substance are dissolved in 100 grams of the solution, and d is the density of the solution, then

$$[a] = \frac{100 \, . \, a}{wdl} \quad \text{and} \quad [m] = \frac{ma}{wdl}.$$

It may be noted here that organic substances which rotate the plane of polarised light contain an asymmetric atom. The elements which furnish such optically active asymmetric atoms are usually carbon and nitrogen, although asymmetric tin, silicon and sulphur atoms have been found to furnish optically active compounds. An asymmetric carbon atom is one to which four different groups or atoms are attached. Quite recently, however, Pope and Perkin have discovered an optically active compound which, although it has no asymmetric atom, yet it has an asymmetric structure.

The rotatory power of an organic liquid is determined by means of a polarimeter, and, of the many forms which have been constructed, the half-shadow instruments of Lippich and Laurent are best suited to the present purpose.

The Laurent polarimeter is represented in diagrammatic form in Fig. 46, and consists of two metal tubes A and B, which are fixed rigidly on a stand and separated by a space in which the observation tube O, containing the active liquid or solution, can be placed.

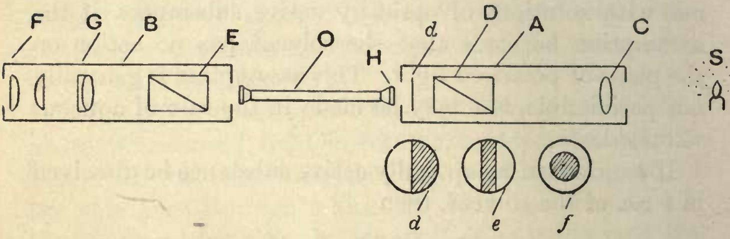

FIG. 46.

The tube A carries a lens C which renders the light coming from the source S parallel, the light then passes on to the Nicol prism D which polarises it; this Nicol is termed the polariser. The light then passes through the observation tube O, and into the second tube B, which has a second Nicol prism E, termed the analyser, and a telescope FG, contained in its length. At H, the opening of the tube A is half covered by a semicircular plate of quartz *d*, cut of such a thickness that the phase of the light passing through it is changed by half a wave length. If the optical axis of the quartz plate is parallel with the plane of polarisation, then no effect will be observed in the telescope due to half the light passing through the quartz plate, *i.e.* the intensity of the light in both halves of the field will be the same. On the other hand, if the polariser is turned through an angle δ, then that portion of the light which passes through the quartz plate will be rotated by an equal amount in the opposite direction, *i.e.* there will be two beams of polarised light emerging from the tube A, whose planes are inclined at an angle 2δ to one another. On observing the light through the telescope, one-half of the field will be dark and the other half light; if the analyser be now rotated the light and dark halves will interchange. There is, however, an intermediate position at which both halves of the field are uniformly illuminated, and this is the position at which all observations are made. The angle 2δ is termed the "half-shadow angle," and it can be made larger or smaller by rotating the polariser. By diminishing the half shadow angle, the sensitiveness of the instrument can be increased, but with increasing sensitiveness a difficulty arises in deciding when the field is uniformly illuminated. In practice it is found that a half-shadow angle of 4°–6° is most suitable. This ought, however, to be fixed by the operator himself, so that he can decide when the field is uniformly illuminated without unduly straining the eye.

In many modern instruments the half shadow is produced by having a strip of quartz *e* (Fig. 46) instead of a semicircle; this divides up the field into three parts, the two outer of which are light, whilst the inner one is dark, and *vice versa*. This arrangement facilitates the finding of the position of equal illumination. A third means of producing the shadow is to use a small circular piece of quartz *f* (Fig. 46); the effect in this case is to produce a dark centre surrounded by a bright ring, or a black ring round a bright centre. The Lippich polarimeter differs from the Laurent instrument in having instead of the quartz plate a small Nicol prism, which covers half of the opening at the end of the polariser tube. This produces exactly the same effect as the quartz plate, but it has the advantage that it may be used for light of any wave length, whereas the Laurent polarimeter must always be used with light of the one definite wave length for which it has been constructed.

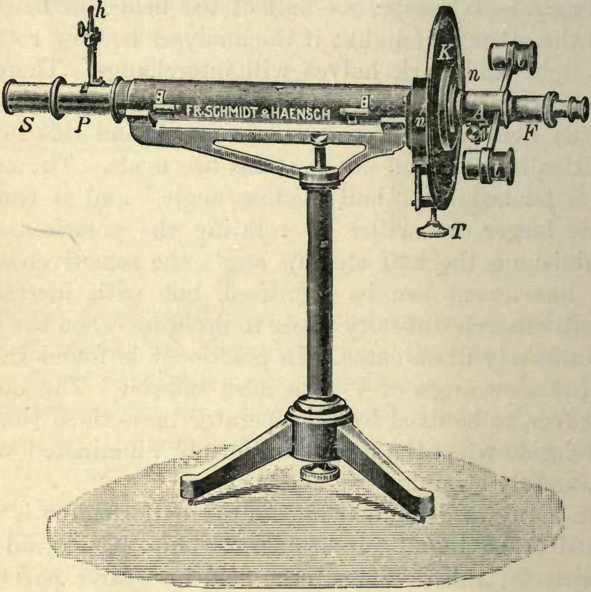

Fig. 47.

The general outside appearance of the Laurent polarimeter is illustrated in Fig. 47. The end S is directed towards the source of light, and contains the lens for rendering the beam parallel, and the light filter, which consists usually of a thin slab of potassium bichromate.

The polariser is situated at P, and is attached to a small lever *h*, by means of which it can be rotated and the half shadow angle changed. The lever *h* moves over a small graduated scale, which indicates the amount the polariser has been rotated. The observation tube is placed in a groove situated in the centre of the apparatus, and protected from extraneous light by means of a hinged cover. The analyser is situated at A, and is connected by means of a small lever to the screw just below A, this is used for moving the analyser independently from the scale, and is used to adjust the zero of the instrument. The analyser tube, containing the telescope F, is attached to a graduated scale K, the whole of which, together with the analyser, can be rotated past fixed verniers n and n_1 by means of a rack and pinion arrangement T. Two reading lenses *l* are attached on a free moving arm, to facilitate the reading of the vernier. In most polarimeters, it will be found that the graduated circle is divided into degrees and quarters of a degree, and the vernier is divided into twenty-five parts which are equal to twenty-four of the quarter degree divisions of the circle, so that each division on the vernier scale is equal to 0°·01.

It has already been noticed that monochromatic light must be used for experiments on optical rotation. Most instruments of the Laurent type are constructed for use with sodium light. A steady sodium flame of fairly constant intensity may be obtained in the following manner. An ordinary bunsen burner provided with a metal screen is used. A small cage made of platinum gauze is suspended by a piece of stout platinum wire stretched across the top of the screen, so that the cage just touches the edge of the flame at the height of the blue inner cone. A few pieces of fused sodium bromide are placed in the cage, and they are replenished from time to time. Another method for producing an intense sodium flame consists in allowing a bunsen flame to pass through a hole in a piece of asbestos board; near the hole a small heap of sodium chloride is placed, which must be replenished from time to time. The flame must just touch the edge of the hole, and be so arranged that about one-third of it is above the asbestos.

The tubes in which the liquids are measured are made of stout glass, with accurately ground ends; thin circular plates of glass serve to close the ends of the tube. These are secured by metal screw caps and rubber washers. Fig. 48 illustrates the observation tube.

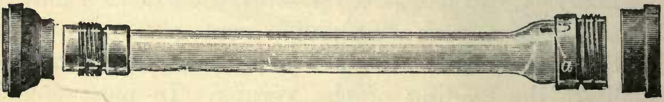

FIG. 48.

These are generally made in lengths which are multiples of a decimetre, since this is the unit of length in polarimetric determinations. The usual lengths are 0·5, 1 and 2 decimetres. For maintaining constant temperature during observations, the tubes are fitted into rectangular metal boxes, which are lined outside with asbestos. These can be filled with water and maintained at any given temperature. Another method of maintaining the temperature constant is to enclose the tube in a wider glass tube, and circulate water at constant temperature through it by means of two side tubes, after the manner of the outer jacket of a Liebig condenser. Fig. 49 illustrates the two methods of maintaining the temperature constant. For ordinary purposes, however, the simple tube is sufficient, since specific rotation does not vary much with temperature. Before making a measurement the polarimeter must be adjusted. First of all the half-shadow angle must be adjusted so that

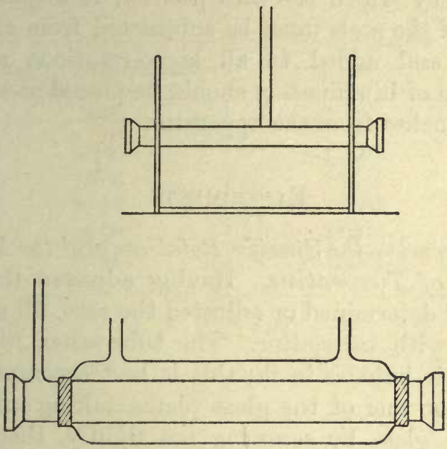

FIG. 49.

the operator is easily able to distinguish the position of equal illumination of the field. This being accomplished, and the polarising prism fixed in position, the zero must next be adjusted, or, in the case of those instruments which are unprovided with means of adjusting the zero, it must be noted. To determine the zero position, one of the measuring tubes is filled with distilled water and placed in position, and the position of equal illumination found and noted. Several determinations should be made, approaching the position from either side. The analyser may then be moved to adjust[1] the zero of the scale to this position, if the instrument in question is provided with means of adjustment, if not, then all subsequent readings must be corrected for the displacement of the zero, *i.e.* the angle by which the zero position is displaced from the zero of the scale must be subtracted from all dextro-rotations and added to all laevo-rotations measured. The source of illumination should be placed at a distance of 4 to 6 inches from the apparatus.

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[1] It is recommended that the analyser should not be removed, *i.e.* that the zero should not be adjusted, for it often happens that moving the analyser by an unskilled person throws the instrument permanently out of adjustment.

EXPERIMENTS

(i) *Determine the Specific Rotation and the Molecular Rotation of Turpentine.* Having adjusted the polarimeter and determined or adjusted the zero, fill a measuring tube with turpentine. The tube when filled must have no air bubbles in it; this is best accomplished by screwing on one of the glass plates, taking care not to strain the glass by screwing too tightly, then fill the tube to overflowing and slide on the other plate, and then, keeping the tube still in a vertical position, screw on the metal cap, again taking care not to screw too tightly. Clean the ends of the tube and measure the angle of rotation as described above. The results must be given expressing the temperature of observation and the wave length of the light used, thus $[a]_{D}^{t°}$, $[m]_{D}^{t°}$. Before the result can be calculated, the density of turpentine at the temperature of the experiment must be determined. For method of determining this, see Chapter V.

(ii) *Determine the Specific Rotation of Tartaric Acid at* 20°. Make up a solution of tartaric acid of about 10 per cent. strength, by weighing out to the nearest milligram about 10 grams of tartaric acid, and making it up to 100 c.c. of solution in water. Fill a measuring tube and determine the rotation. The density of tartaric acid solution at 20° is given in the following table.

By drawing a curve of the density and concentration, the density of the solution used may be obtained by interpolation.

Weight of Tartaric Acid per 100 c.c. Solution.	d_4^{20}.
20·70	1·0978
16·06	1·0747
10·89	1·0491
5·09	1·0215
2·01	1·0074

CHAPTER XI

SPECTROSCOPY

1. Emission Spectra. When a beam of white light, from an incandescent solid, is allowed to pass through a glass prism, and the emerging beam is examined, it is found to consist of a continuous band of coloured light ranging from violet to red. If, instead of a beam of white light, from an incandescent solid, the light emitted by an incandescent gas or vapour be substituted, the emergent beam will be found to consist of a few differently coloured lines or bands isolated from one another by dark spaces. These bands or lines constitute the spectrum of the substance emitting the light, and they are characteristic of that substance both as regards number and colour. They have perfectly defined positions with respect to one another, *i.e.* they have definite wave lengths, which are not influenced in any way by the presence of lines due to other substances. It becomes possible, therefore, from the position of the lines emitted by an unknown substance, to specify its nature, and, as will be seen later, it is not only possible to determine the nature of the substance emitting the light, but also, in the case of organic compounds, by a slight modification of the process, to draw conclusions about the constitution of the molecule of organic substances. It is the usual practice in spectroscopic determinations not to make a measurement of the actual wave length of the various lines, but to obtain this either by comparison with lines of known wave length or by interpolation on curves prepared for the instrument being used.

The apparatus used for examining the light emitted by incandescent substances is termed a spectrometer. Fig. 50 shows a simple form, it consists of a metal tube C, termed the collimator, which carries a slit S at one end; this is adjustable and serves to admit a narrow band of light. At the other end of the collimator there is fixed a lens *l*, which serves to render parallel the beam of light admitted by S. The collimator is fixed to a circular table T, which is graduated in degrees and thirds of a degree. A telescope F is also attached to the table, but in such a way that it may be rotated about the table. Attached to the telescope is a vernier divided into divisions which are of such a size that twenty are equal to nineteen of the smaller divisions on the table, *i.e.* one division is equal to 1′ of arc. The vernier slides above the table as the telescope is moved round. Between the collimator and the telescope, on a raised movable platform, a heavy glass prism P is placed. In larger instruments, for the purpose of obtaining greater dispersion,

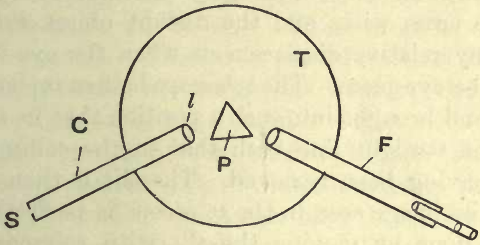


FIG. 50.

two or more prisms are used, which are so arranged round the graduated circle that the light passes through them successively. A spectrometer must always be adjusted before use. To do this the telescope is unscrewed and removed from its support, and the cross wires are brought into sharp focus by moving the eye-piece. Then the telescope is directed toward some distant object, *e.g.* telegraph wires, and these are brought into focus by moving the tube containing the eye-piece and cross wires. By this means the telescope is focussed for parallel rays, *i.e.* for light proceeding from infinity, and, if the focussing has been correctly carried out, the cross wires and the distant object should not show any relative displacement when the eye is moved across the eye-piece. The telescope is then replaced in its holder and brought into such a position that its axis is in the same straight line with that of the collimator, the prism having been removed. The slit is then adjusted so that its image seen in the telescope is perfectly sharp. This is done by moving the slit with reference to its distance from the collimator lens. When the image is quite sharp, the light entering the telescope is known to be parallel, since the telescope has been adjusted for parallel light. The prism is now replaced with its refracting edge parallel to the slit, and the slit is illuminated with a sodium flame placed three to four inches away. The prism and space between the collimator and telescope are covered by a black cloth, to cut off all extraneous light, and the telescope is moved round the scale until a yellow image of the slit occupies the middle of the field. The prism is then slowly rotated, and the image of the slit observed through the telescope. The image will be seen to advance slowly across the field up to a certain point, at which it commences to retrace its path. This position is carefully ascertained, and the prism fixed when the image of the slit occupies this stationary place. This is the position of minimum deviation of the prism, and the one which the prism must have in all determinations.

Having adjusted the instrument in the way described, a curve or map may be constructed, by means of which the wave lengths of the lines of unknown substances may be determined.

To do this, the slit is illuminated with the light from a known incandescent vapour, and, on observing the spectrum through the telescope, the lines of this particular substance will be seen. These must be measured one by one; the telescope is moved so that the intersection of the cross wires coincides with a given line, and then it is clamped and the angular deviation is read off, the other lines are then treated in the same way. When some ten or fifteen lines, covering the whole range of the visible spectrum, have been measured in this way, the angular readings are plotted as abscissae against the corresponding wave lengths as ordinates, and a smooth curve is drawn through them. If, now, the light of an unknown substance be observed in the spectrometer from the angular deviations of its various lines, the wave lengths may be obtained by means of the curve, and, by use of a table of wave lengths, the nature of the unknown substance determined. In making such a calibration curve, only strong and well defined lines should be used. Collie has shown (*Proc. Roy. Soc.* 71, 25, 1902) that if hydrogen and helium are mixed with a little mercury vapour in a vacuum tube, a number of the mercury lines are strengthened, and he recommends the use of such a tube for the preparation of a calibration curve.

Failing a tube of this nature, the lines of hydrogen and helium should be used to make the curve. A curve produced in this manner is only of use for the instrument with which it has been constructed, and must not be used for any other. In making measurements, care must be especially taken not to apply any pressure to the telescope, for this may change the relative position of the cross wires to the rest of the instrument, and so produce errors in the angular deviation. Below is given a list of the principal lines seen in a Collie tube.

Element.	Colour of Line.	Wave Length in Ångström Units $=10^{-7}$ mm.
Helium, - - -	Red	7065·5
Helium, - - -	Red	6678·4
Hydrogen, - -	Red	6563·0
Mercury, - - -	Orange	6152·0
Helium, - - -	Yellow	5875·9
Mercury, - - -	Yellow	5790·5
Mercury, - - -	Yellow	5767·5
Mercury, - - -	Green	5461·0
Helium, - - -	Green	5015·7
Helium, - - -	Green	4922·0
Hydrogen, - -	Blue	4861·5
Helium, - - -	Blue	4713·3
Helium, - - -	Violet	4471·6
Mercury, - - -	Violet	4358·6
Hydrogen, - -	Violet	4340·7

Instead of using an angular deviation calibration curve, a fixed scale may be employed. This is contained in a third tube H (Fig. 51), which is fixed to the spectrometer table in such a position that the image of the scale, illuminated by a small electric lamp, is reflected from the face of the prism into the telescope, and appears superposed upon the lines. The illumination of the scale should not be very strong, or otherwise weak spectrum lines will be rendered invisible; the illumination may be varied by altering the distance of the lamp from the scale. The scale is adjusted by illuminating the spectrometer slit with a sodium flame, and bringing the sodium line well into the middle of the field. Then the scale is sharply focussed, and the telescope fixed so that the sodium line is in the middle of the scale. A series of lines of known wave length, covering the whole of the visible spectrum, is measured in scale divisions. The scale divisions are then plotted as abscissae against the wave lengths as ordinates, and a smooth curve is drawn through the points as in the last case. The same series of hydrogen, helium and mercury lines may be used, but generally the former method of calibration is more accurate than this one, and is to be preferred.

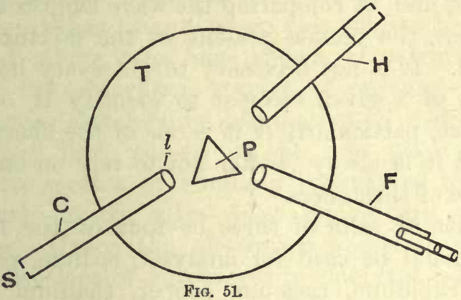


FIG. 51.

EXPERIMENT

Determine the Metals contained in a Given Mixture. Before commencing the analysis of the mixtures, a curve must be prepared by one of the above methods. The mixtures for analysis are introduced into a bunsen flame in a small platinum cage, similar to that described in the production of a sodium flame (Chap. X.). Generally the light emitted by these substances is of an evanescent nature, but it may be revived by moistening with hydrochloric acid. An alternative method of procedure is to make a solution of the mixture, and lead it from a glass tube into the flame by means of an asbestos fibre. The deviation of each of the lines must then be carefully measured, and their wave lengths interpolated from the curve which has already been prepared. A list of the wave lengths of the lines of the metals which can be obtained from a bunsen flame, is given in Table VII. Appendix, and, by comparing the wave lengths measured with these, the metals present in the mixture can be identified. It is not necessary to get every line of the spectrum of a given element to identify it, one alone will suffice, particularly if it is one of the characteristic lines, but it is always better not to rely on one line in a mixture of substances.

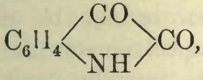
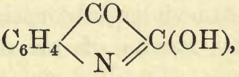
Mixtures of salts of three or four of the following metals should be used for analysis: sodium, potassium, lithium, rubidium, caesium, copper, thallium, calcium, barium, strontium and indium.

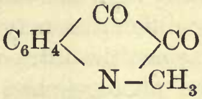
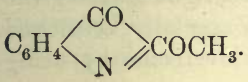
The spectra of other metals are obtained by volatilising the salts by means of a stream of electric sparks. For information on this subject the reader is referred to works on Spectroscopy.

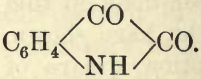
2. **Absorption Spectra.** When a beam of white light, which has passed through a coloured solution, *e.g.* dilute potassium permanganate solution, is examined in a spectroscope, a continuous spectrum is obtained which is crossed by a number of dark bands. A portion of the light has been absorbed in its passage through the solution. Such a spectrum is termed an "absorption spectrum." If, instead of passing white light through

a solution, it is passed through an incandescent vapour or gas, a spectrum will be obtained which is crossed by a number of black lines termed "Fraunhofer" lines. These lines occupy the same positions as the corresponding bright lines of the emission spectrum of the gas. Hence the absorption spectrum is just as characteristic of a substance as its emission spectrum, and it is due, in the same way as the emission spectrum, to the vibrations of the atoms or molecules, or both, of that substance. Hence it is obvious that a careful study of the absorption spectra of liquids and solutions may lead to valuable information with regard to their constitution. A great deal of work has been done on this subject by Hartley, Baly and others, who have shown abundantly, that a study of the absorption spectra of organic substances leads to clear and definite information on their constitution. They have shown in the first place, that the absorption spectra of similarly constituted substances, particularly in the ultra-violet region, are similar in character. Hence the absorption spectrum can settle the constitutions of substances in doubtful cases. This will probably be clearer if a definite case is considered.

Purely chemical evidence leaves a doubt as to whether isatin has a constitution represented by

 or by 

i.e. whether it is the lactam or the lactime of ortho-amido-phenyl-glyoxylic acid. Isatin gives rise to two methyl ethers whose constitutions are perfectly well known, viz. the N-ether  and the O-ether . The N-ether is similarly constituted to the lactam of ortho-amido-phenyl-glyoxylic acid, and the O-ether to the lactime. Hence, if the ultra-violet absorption spectra of solutions of the two ethers and of isatin itself be examined, one or other of the ethers should have an absorption spectrum similar in character to that of isatin. Hartley carried out this investigation and found that the N-ether and isatin had similar absorption spectra, whilst that of the O-ether was entirely different. Hence, since similarly constituted compounds have similar absorption spectra, it follows that isatin is the lactam of ortho-amido-phenyl-glyoxylic acid, *i.e.* it has the constitution expressed by



Experimental details for obtaining Absorption Spectra. The source of light to be used in such determinations must be very rich in ultra-violet rays, and on this account, Hartley makes use of the light from electric sparks passing between electrodes of a cadmium, tin, lead alloy, whilst Baly uses the light from an arc passing between iron pencils. The latter method is the easier to manipulate, and gives a more intense light, and for these reasons is to be recommended. The measurement of ultra-violet absorption spectra cannot be carried out by means of an ordinary spectrometer for two reasons: (1) ultra-violet rays are invisible, and consequently the eye is useless in such determinations for directly reading off the position of the absorption bands; and (2) ultra-violet rays are largely absorbed by glass. The first of these difficulties may be overcome by the aid of photography, since the ultra-violet light entering the telescope may be photographed on specially sensitised plates, and the second difficulty is overcome by using a spectrometer with prisms and lenses of quartz, or better, fluorite, both of which allow ultra-violet rays to pass through them, the former down to wave lengths of 248 $\mu\mu$ and the latter to 185 $\mu\mu$. The apparatus employed for photographing ultra-violet spectra is termed a spectrograph, and is illustrated in Fig. 52. It consists of a spectrometer fitted with quartz lenses and a quartz prism, but differs from the ordinary spectrometer in having a photographic attachment instead of an eyepiece. These instruments are constructed so that the whole of the spectrum from 200 $\mu\mu$ to 800 $\mu\mu$ is focussed on to the plate in the dark slide, and hence it becomes unnecessary for either tube of the instrument to be movable. The photographic part of the apparatus explains itself in the diagram. The dark slide holder is constructed so that only a narrow horizontal strip of the plate, as wide as the spectrum, is exposed, thus making it possible, by lowering the dark slide, to take a series of photographs on one plate. The graduated scale on the slide holder is to allow the movement of the plate to be done accurately, and to prevent the overlapping of the spectra. Scales of wave lengths are supplied by the makers with spectrographs of this type, and as these are photographed on glass, the wave lengths of any lines or bands may be directly read off by laying the scale over the experimental photograph. A spectrograph may obviously be used for photographing an emission spectrum, by illuminating the slit in the ordinary way and exposing the plate. The time of exposure can only be determined by experiment, and depends much on the instrument. As a rough guide the following figures, given by the makers of the instrument illustrated in Fig. 52, may be used. Using Lumière ordinary plates, and an iron arc as the source of light, about 3 seconds exposure will be sufficient; with a cadmium spark illumination 45 seconds, and with a hydrogen end-on tube about 1½ minutes. Longer exposures will be required for vacuum tubes of the ordinary types, and for spectra in the red end, specially sensitised plates and long exposures are necessary.

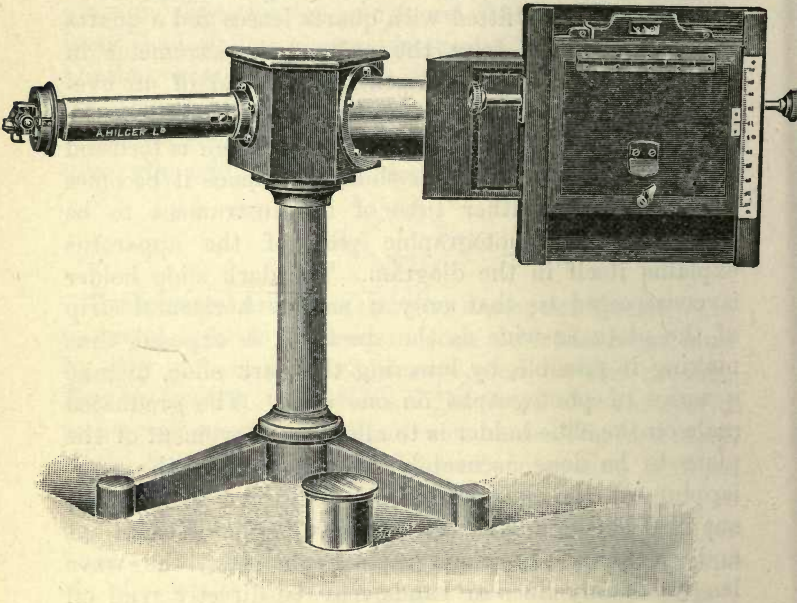


FIG. 52.

Absorption spectra for general purposes, are determined similarly to emission spectra, by allowing light, generally from an iron arc, to enter the slit of the spectrometer after it has passed through the liquid or gas whose absorption spectrum is to be determined. Absorption spectra, which are to be used for determining the structure of organic substances are, however, obtained in a somewhat different manner.

In this case it is not only the number and position of the absorption bands which have to be taken into consideration, but also the persistence of the bands with dilution of the solution containing the substance through which the light passes. Hence, to make an examination of the absorption spectrum of an organic substance, with the object of gaining insight into its constitution, it is necessary to photograph the absorption spectra of a large number of increasingly dilute solutions of the substance, until complete transmission of the light is obtained. This method of treating the absorption spectra is due to Hartley, as also is the method of expressing the results of the experiments. A slightly modified and improved method of expression due to Baly and Desch (*J.C.S.* 85, 1039, 1904) will be described here. The wave lengths of the absorption bands are plotted as abscissae against the logarithms of the relative thicknesses of the solution as ordinates. When complete transmission is obtained, the points are connected up, and an undulating curve is obtained, in which the space in each hollow represents the region of an absorption band together with its persistence on dilution.

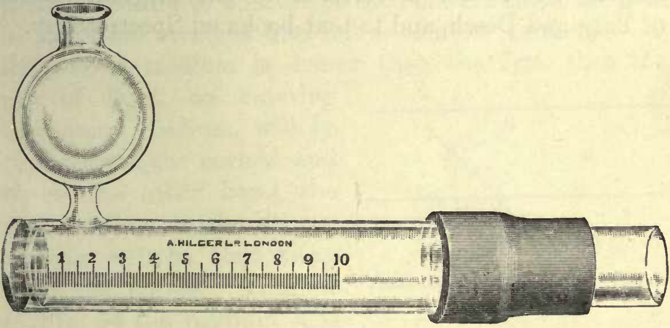


FIG. 53.

The variation of the thickness of the layer of the liquid is best effected by the Baly absorption tube (Fig. 53). It consists of two glass tubes which fit loosely inside one another. The ends of these are closed by quartz plates which are cemented on. The outer tube is fitted with a small bulb funnel, and is carefully graduated in millimetres. The apparatus is made water-tight by a piece of rubber tubing, which allows the inner tube to be drawn out when the length of the column of liquid is to be varied. For further details on this subject, the reader is referred to the original papers of Baly and Desch, and to text-books on Spectroscopy.

CHAPTER XII

REFRACTIVITY

WHEN an oblique ray of light passes from one transparent medium to another, it does not continue its path in the same straight line, but is bent or refracted. If the second medium is denser than the first, then the ray of light, on entering the second medium, will be bent toward the normal, and if, on the other hand, the first medium is the denser, the ray will be bent away from the normal. Thus, if in Fig. 54 the medium A is the less dense, then a beam of light will follow the path indicated in the diagram; and if i represent the angle of incidence, and r the angle of refraction, μ_1 the index of refraction of the medium A, and μ_2 that of B, then the ratio between the coefficients of refraction in the two media will be given by the expression

$$\frac{\sin i}{\sin r}=\frac{\mu_1}{\mu_2}.$$

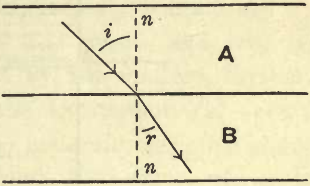


FIG. 54.

The angle of refraction will increase as the angle of incidence is increased, until the angle of incidence is 90°, i.e. $\sin i=1$. When this is the case

$$\sin r=\frac{\mu_2}{\mu_1}.$$

Since light of different wave lengths is refracted differently, the determination of the value of μ is usually carried out with monochromatic light, and the wave length of the light employed is always stated with the experimental results.

In physical chemistry the refractive indices of liquids have often to be determined. The measurements are made by means of the principle stated above, where the liquid in question constitutes one medium, generally the less dense, and a dense right-angled glass prism of known refractive index, greater than that of the liquid, the other. The liquid B (Fig. 55) is placed in a glass cell, which is cemented on to the top of the heavy glass prism C. A beam of monochromatic light, focussed on to the liquid, will pass into the prism and be refracted as indicated in the diagram, and as it emerges from the prism it will be received into a telescope, by means of which the angle at which it emerges from the prism can be measured.

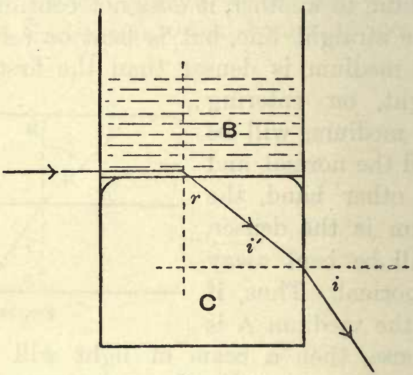


FIG. 55.

If the ray with largest incident angle to enter the prism, *i.e.* 90°, be considered, this ray will be the one which sharply marks off the dark region from the light region, and is the one used for all determinations of refractive index.

For this ray, since $sin\, i=1$,

$$sin\, r=\frac{\mu_2}{\mu_1},$$

where μ_2 and μ_1 are the indices of refraction of the liquid and the prism respectively. This beam further leaves the prism at an angle i' and travels on in the air at an angle i. For this, the expression

$$\frac{sin\, i}{sin\, i'}=\mu_1,$$

since the refractive index of air is unity. Combining these expressions, the equation $\mu_2=\sqrt{\mu_1^2-sin^2 i}$ is obtained.

The value of μ_1 is that of the prism, and will be provided with the instrument by the makers, further, tables giving the value of the expression $\sqrt{\mu_1^2-sin^2 i}$ for various values of i, are also generally supplied along with the refractometer, so that the value of μ_2 is directly obtained from the tables by looking up the value of $\sqrt{\mu_1^2-sin^2 i}$ for the measured value of i.

Although the refractive index must always first be determined, yet it is comparatively little used for physico-chemical purposes, two derived functions, the *Specific Refractivity* and the *Molecular Refractivity*, being more generally employed. These functions have an additional advantage, for whereas the refractive index varies somewhat with temperature, they are practically constant.

There are two expressions for the specific refractivity: the first, due to Gladstone and Dale, is $\mathsf{R}=\frac{\mu-1}{d}$, and the second, due to Lorentz and Lorenz, is $\mathsf{R}_1=\frac{\mu^2-1}{\mu^2+2}\cdot\frac{1}{d}$;

and corresponding to these there are similarly two expressions for the molecular refractivity:

$$\mathrm{M} = \frac{\mu - 1}{d} \cdot m \quad \text{and} \quad \mathrm{M}_1 = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{m}{d},$$

where R and R_1 represent the specific refractivities, M and M_1 the molecular refractivities, m the molecular weight and d the density of the substance in question.

The measurement of the refractive index, as has already been stated, must be carried out with monochromatic light. For this purpose the sodium flame, or the light from a vacuum tube containing hydrogen, is generally used. In the case of hydrogen light, the red line (C) or the blue line (F) is used in the measurement. Occasionally the thallium or the lithium flame is employed. If the thallium flame be used, it is necessary that it should be placed under a hood, or so arranged that the poisonous vapours of the thallium compound are removed. This is easily accomplished by supporting a large inverted funnel over the flame at a height of about 6–8 inches from the flame. The funnel is then connected to a water pump, and the fumes are drawn away with the air current which is thus generated.

The light used in the experiments must be as intensive as possible. The flames of sodium, lithium and thallium may be obtained as described in Chapter X. The hydrogen light is best obtained from an "end-on" vacuum tube (see Fig. 56). This type of Geissler tube gives the intensity of illumination which is so often lacking when ordinary straight vacuum tubes are used. The measurements are generally carried out by means of a Pulfrich refractometer (Fig. 56). This consists of a heavy glass prism L surrounded on all sides but the one nearest to the telescope by a metal jacket, and which carries on its upper side, the glass cell into

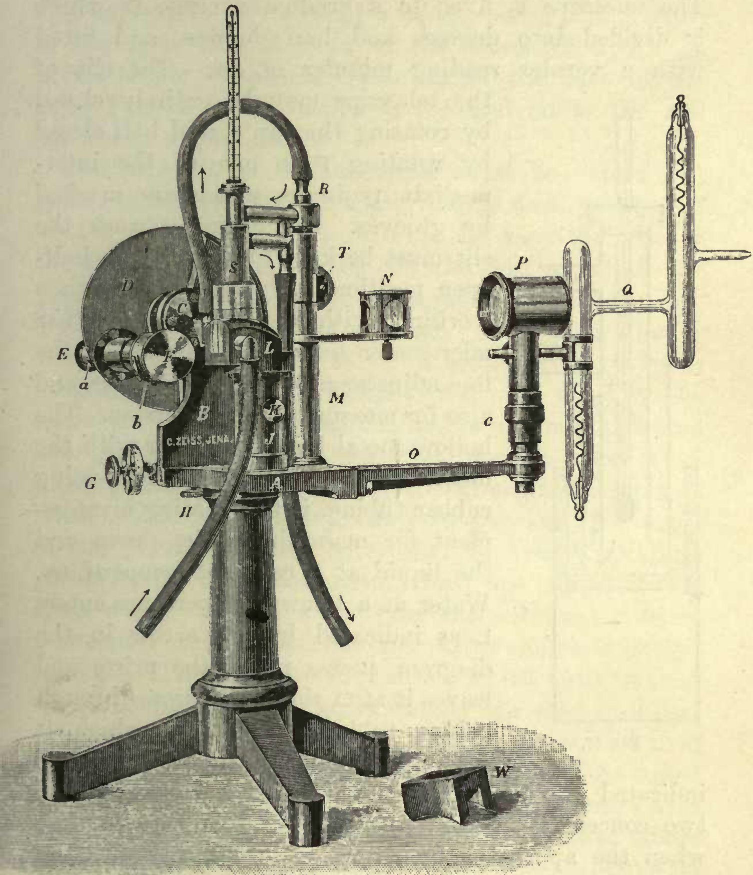


FIG. 56.

which the liquid under observation is placed. The prism is in such a position that the light which emerges from it enters the telescope **EF** by means of the slit *b*, and is reflected along the axis of the telescope. The telescope is fixed to a graduated circle **D**, which is divided into degrees and half degrees, and fitted with a vernier reading minutes of arc. The slit of the telescope may be entirely closed by rotating the cap **F**, and half closed by rotating **F** to one of the intermediate positions which are marked by grooves. For ordinary work the slit must be kept fully open, the half-open positions only being used when working with a divided cell. The micrometer screw **G** is for use in the fine adjustment of the cross wires, and also for measuring the dispersion. The hollow metal box **L**, together with the metal tubes **SR** and their connecting rubber tubing, is the heating arrangement for maintaining the prism and the liquid at a constant temperature. Water at a known temperature enters **L** as indicated by the arrow in the diagram, passes round the prism and leaves it at **C**, thence it passes through rubber tubing to **R**, from which it enters **S**, leaving by the other tube as indicated in the diagram. The heater **S** is composed of two concentric metal boxes, as shown in Fig. 57, and when the apparatus is in use, it is lowered into the liquid by means of the screw **T**. The temperature of the liquid is given by the thermometer screwed into the top of **S**. The apparatus, as illustrated, is arranged for use with light from flames or from vacuum tubes.

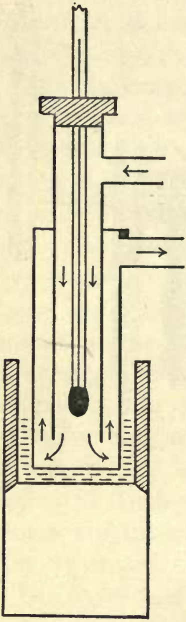


FIG. 57.

The reflecting prism N serves to throw light from a flame on to the side of the cell containing the liquid; it is adjustable by means of a handle beneath it. When a hydrogen tube is used as the source of light, the prism N can be swung back out of the path of the light from the tube which is focussed on to the cell by means of the lens P.

The zero of the refractometer must be determined before measurements are made; this is done by the aid of a small right-angled prism *a* let into the side of the telescope. The vernier and the disc to which the telescope is attached are brought so that the zero division of both almost coincide. Then the disc is clamped by the screw H. The small prism is then illuminated by a strong light, and the field in the telescope will then show the prism on one side and a bright image of it on the other, and the cross wires passing across the field and over the image of the prism. If the telescope is not in its zero position, the image of the prism will also be crossed by two black lines parallel with the cross wires, which are images of the cross wires. If this is the case, the micrometer screw G is slowly turned until the cross wires and their images coincide. This is the zero position, which must be read on the vernier, and if, as is usually the case, it differs from the zero of the scale, it must be noted and used to correct all subsequent readings. Should it be found impossible to bring both cross wires into coincidence with their respective images at the same time, a state of affairs which will arise if the prism has become twisted from its normal position, the upper wire is first brought into coincidence with its image, and the position read, and then the second wire with its image, and the position again read. The mean of the two readings gives the true zero.

Most refractometers are supplied with the cell for holding the liquid, already cemented on, but occasionally this is not done, and frequently the cells come loose. They may be put on again by coating the top of the prism and the bottom of the cell with a thin layer of fish glue or seccotine. A very good cement, and one which is not softened by water, is made by just melting gelatine and then mixing it with a dilute solution of potassium bichromate. The bichromate is then all washed away and the gelatine applied in a very thin layer as described above. Care must always be taken, when putting a cell on to a prism, to see that the layer of cement is uniform.

EXPERIMENT

Determine the Refractive Index of Ethyl Alcohol at 20° *for Sodium Light, and also for the* C *and* F *lines of Hydrogen. Calculate the Specific and Molecular Refractivities.* Place the refractometer in position and determine its zero by the method indicated above. Then wash out the cell by placing about 5 c.c. of absolute alcohol into it, and removing it with a pipette, taking care not to scratch the bottom of the cell with the point of the pipette. Place in two further quantities of alcohol and remove them as before. Then add sufficient alcohol to cover the bottom of the cell to a depth of about 5–6 mm., set the heating water flowing through the heater LS and then lower S into the alcohol. Most instruments are so constructed that S cannot be lowered too far, but care must be taken that there is always a layer of liquid between it and the bottom of the cell. A stream of water at constant temperature is best obtained by placing a coil of lead gas pipe into a large thermostat, and allowing the water to pass slowly through it, and from it to the apparatus. Such a heating coil can be made by winding about 20–30 feet of lead gas piping round a Winchester quart bottle and bringing the bottom end of the pipe up through the centre of the coil. When the temperature in **S** is constant, the measurement may be made. Place a sodium flame about 1–2 feet away from the prism **N**, and turn the prism so that the light is reflected on to the side of the cell. The large prism of the refractometer should now be covered by the wooden cap **W**, which should be kept there during all the measurements. Rotate the telescope and disc until the refracted beam is visible, the field will then be seen to be crossed by a sharply defined band of yellow light. Move the disc and telescope until the intersection of the cross wires is almost coincident with the edge of the yellow light, then clamp the disc by means of the screw **H**, and adjust the intersection of the wires so that it is exactly coincident with the edge of the yellow light, by means of the micrometer screw **G**. Read the angle on the disc. Make several determinations of this angle, approaching it from both sides, and take the mean of the readings. The individual readings should not differ by more than one minute of arc from the mean value. Having thus determined the angle of emergence of the light, the refractive index can be obtained from the formula

$$\mu = \sqrt{\mu_1^2 - sin^2 i},$$

where μ_1 is the refractive index of the prism. The values of $\sqrt{\mu_1^2 - sin^2 i}$ are generally given for varying values of i in tables supplied by the manufacturers with the refractometer. In general these values are given for, one temperature only, viz. 20°, but there is also a table of corrections supplied, for use when temperatures other than 20° have been employed in the determination.

Having thus obtained the refractive index, the specific and molecular refractivities may be calculated from it. The density of alcohol at the temperature of the experiment must be determined as indicated in Chapter V. Calculate the values of M and R, using the formulae:

$$\mathrm{R}=\frac{\mu-1}{d} \quad \text{and} \quad \mathrm{R}_1=\frac{\mu^2-1}{\mu^2+2}\cdot\frac{1}{d},$$

$$\mathrm{M}=\frac{\mu-1}{d}\cdot m \quad \text{and} \quad \mathrm{M}_1=\frac{\mu^2-1}{\mu^2+2}\cdot\frac{m}{d}.$$

Compare the values obtained.

The method of procedure, when using the C and F lines, is practically the same as the foregoing. Clamp the vacuum tube in front of the lens P as indicated in Fig. 56, then focus the light on to the side of the cell, and adjust the position of the vacuum tube so that the lines appear bright and clear in the telescope. When the lines have been obtained bright and clear, narrow them down by closing the diaphragm attached to the lens P. Two bright lines, the red (C) and the blue (F) will be most conspicuous. Now rotate the disc until the intersection of the cross wires almost coincides with the red line, clamp the disc and bring the intersection of wires into coincidence with the line by means of the micrometer screw G, read the angle on the disc. Then, by means of the micrometer screw, bring the wires so that they coincide with the blue line, and read the position again. In making readings for a series of lines, it is only necessary to read the value for the first line on the disc, the others being obtained from the readings of the micrometer screw.

The screw head rotates past a fixed horizontal scale which is divided into degrees and thirds of a degree. It is divided into 200 divisions, and one complete revolution of the screw advances it one of the small divisions of the horizontal scale, *i.e.* twenty minutes, hence one division of the screw head represents one-tenth of a minute of arc.

Calculate the specific and molecular refractivities for the C and F lines, using both formulae, as for the case of the sodium line.

Atomic Refractivity

Refractivity has been shown to be largely an additive property, made up, in the case of molecular refractivity, of the sum of the refractivities of the constituent atoms, *i.e.* the atomic refractivities. Consequently, when the atomic refractivities are known, the molecular refractivity may be calculated from them, and *vice versa* the atomic refractivites may be deduced from the molecular refractivities of a series of compounds containing these atoms.

Thus the molecular refractivity M of a compound may in general be represented by an expression

$$\mathrm{M} = (n\mathrm{C} + m\mathrm{H} + p\mathrm{O} \ldots),$$

where C, H and O represent the atomic refractivities of the elements carbon, hydrogen and oxygen respectively, and n, m, and p the number of these atoms respectively present in the given compound. Definite values have also been attributed to double and triple linkages, and oxygen has different values in different types of compounds.

EXPERIMENT

Determine the Atomic Refractivities of Carbon, Hydrogen, Bromine and Oxygen (hydroxylic). Determine the molecular refractivities of methyl alcohol, ethyl alcohol, ethyl bromide and ethylene dibromide at the same temperature, by the method already described, using the same source of light in each case. Now let m_1, m_2, m_3 and m_4 be the values obtained in the four cases respectively. Then, since it may be assumed that the refractive power is an additive property, and using the chemical symbols of the elements to represent their refractivities,

$$C_2H_5OH - CH_3OH = CH_2$$

i.e. $m_2 - m_1$ = the refractivity of CH_2,

$$C_2H_4Br_2 - 2CH_2 = 2Br$$

i.e. $m_4 - 2(m_2 - m_1) = 2 \times$ atomic refractivity of Br.

Hence the atomic refractivity of bromine

$$= \left(\frac{m_4 + 2m_1 - 2m_2}{2}\right).$$

$C_2H_5Br - 2CH_2 - Br = H$ = atomic refractivity of H,

i.e. $m_3 - 2(m_2 - m_1) - (m_4 + 2m_1 - 2m_2) \times \frac{1}{2}$
= atomic refractivity of hydrogen.

$$\text{Hydrogen} = m_3 - m_2 + m_1 - \frac{m_4}{2}.$$

$CH_2 - 2H = C$ = atomic refractivity of carbon.

$(m_2 - m_1) - 2\left(m_3 - m_2 + m_1 - \frac{m_4}{2}\right)$
= atomic refractivity of carbon.

$$\text{Carbon} = 3m_2 - 3m_1 - 2m_3 + m_4.$$

$CH_3OH - CH_2 - 2H = O$ = atomic refractivity of oxygen.

i.e. $m_1 - (m_2 - m_1) - 2\left(m_3 - m_2 + m_1 - \frac{m_4}{2}\right)$
= atomic refractivity of oxygen.

$$\text{Oxygen (hydroxylic)} = m_2 + m_4 - 2m_3.$$

The following additional experiments are suggested for the determination of other atomic refractivities.

(i) *Determine the Atomic Refractivity of Carbon, Hydrogen, Oxygen (ketonic) and Oxygen (hydroxylic).* Use for this experiment methyl alcohol, ethyl alcohol, acetic acid and acetone.

(ii) *Determine the Atomic Refractivity of Chlorine.* Use chloroform and carbon tetrachloride for this experiment, and make use of the values found for carbon and hydrogen in the previous experiments.

Refractivity of Solutions

The refractivity of an homogeneous transparent mixture or solution is the mean of the refractivities of its constituents. Thus if r_1, r_2, r_3 represent the refractivities of the mixture and its two constituents respectively, then

$$r_1 = r_2 \cdot \frac{p}{100} + r_3\left(\frac{100-p}{100}\right),$$

where p represents the percentage of the constituent having the refractivity r_2 in the mixture.

Hence it is possible to determine the refractivity of a substance in solution, by measuring the refractivity of the solution and the solvent. If μ_1, μ_2 and μ_3 be the refractive indices of the solvent, solution and dissolved substance respectively, and d_1, d_2 and d_3 their densities, then

$$\frac{\mu_2 - 1}{d_2} = \frac{\mu_1 - 1}{d_1} \cdot \frac{100-p}{100} + \frac{\mu_3 - 1}{d_3} \cdot \frac{p}{100},$$

where p is the percentage of the dissolved substance contained in the solution.

$$\frac{\mu_3 - 1}{d_3} = \frac{\mu_2 - 1}{d_2} \cdot \frac{100}{p} - \frac{\mu_1 - 1}{d_1} \cdot \frac{100-p}{p},$$

or using the Lorentz and Lorenz formula for the refractivity,

$$\frac{\mu_3^2-1}{\mu_3^2+2}\cdot\frac{1}{d_3}=\frac{\mu_2^2-1}{\mu_2^2+2}\cdot\frac{100}{d_2p}-\frac{\mu_1^2-1}{\mu_1^2+2}\cdot\frac{100-p}{d_1p}.$$

EXPERIMENTS

(i) *Determine the Specific Refractivity and Molecular Refractivity of Potash Alum.* Make a solution of alum containing 5–6 per cent. of alum by weight, and determine its refractive index at about 20°; since the refractive index of air is taken as unity, the refractive index of water must also be determined. Next obtain the density of water and the solution at the temperature of the experiment, either from tables or by experiment. From the data obtained, calculate the specific and molecular refractivities by means of the formulae given above.

(ii) *Determine the Refractivity of a Mixture of Ethyl Alcohol and Methyl Alcohol.* Make a mixture of known weights of methyl and ethyl alcohols, and determine its refractive index at 20°. Calculate the refractivity of the mixture. Assuming the refractivity of one of the constituents, calculate the value of the other, and compare the value obtained with that directly measured. Below is given a table of the refractive indices for methyl and ethyl alcohols, together with their relative densities:

	d^t_4.	Temp.	μ_D	μ_C	μ_F
Methyl Alcohol, -	0·7921	20°	1·3290	1·3275	1·3330
—	0·7961	18°	1·3301	—	—
Ethyl Alcohol, -	0·7899	20°	1·3617	1·3593	1·3653
—	0·8026	18°	1·3619	1·3605	1·3663

CHAPTER XIII

THERMAL MEASUREMENTS

Before thermochemical experiments can be made, certain thermal values of the substances employed must be known; thus, for example, knowledge is always required of the specific heat of the reacting substances, and frequently it is necessary to know two or more of the values: melting point, boiling point, latent heat of fusion and latent heat of vaporisation. The methods of determining these values will therefore be considered here, whilst the "thermochemical" determinations will be considered in Part II. of this work.

1. Determination of Melting Point

In the practice of organic chemistry, it is usual to determine the melting point of a substance by placing a small portion of the substance in a thin-walled capillary tube. The tube is then attached to the stem of a thermometer, so that the substance and the bulb of the thermometer are at the same height; the thermometer is then placed in a bath of sulphuric acid or water, which is gently heated until the substance melts. The temperature at which the substance melts is read off and recorded as the melting point. Such determinations are, however, seldom correct, and vary with the diameter of the capillary tube employed.

For accurate determinations of melting point, a quantity of the substance, 5–6 grams if possible, is placed in a narrow test tube, which is supported by a cork in a second slightly wider test tube, which serves as an air jacket (see Fig. 40, Chapter VII.). The tubes are placed in a bath, which may be raised to a higher temperature than the melting point of the substance. This is provided with a stirrer, and is slowly heated until the substance in the inner tube has melted. When this is the case, a corrected thermometer and a stirrer of platinum wire are placed in the molten substance, and the temperature of the bath is allowed to fall until it is about one degree below the melting point of the substance in the inner tube, and here it is kept stationary. The temperature of the molten substance slowly falls to below its melting point, and suddenly the liquid commences to solidify, and the temperature rises to the melting point. Both the substance itself and the heating bath should be stirred quickly while the temperature is rising. Should the substance not solidify when cooled slightly below its melting point, the addition of a small particle of the solid will bring about solidification.

If any portion of the thermometer thread is outside the tube containing the molten substance, a correction must be applied to obtain the true melting point, viz.

$$\mathsf{T}_{corr} = \mathsf{T} + n(\mathsf{T} - t)0{\cdot}000154,$$

where T is the observed melting point, n the number of degrees of exposed thread and t the mean temperature of the exposed thread. It will be obvious that such a correction only gives a near approximation if long lengths of thread are exposed, and it is always better to use short normal thermometers, where the thread is always inside the melting vessel, for these determinations.

2. Determination of Boiling Point

The normal **Boiling Point** of a liquid is that temperature at which the vapour tension of the liquid becomes equal to 760 mm. of mercury. In its wider and general sense the boiling point may be defined as the temperature at which the vapour tension of a liquid equals the outside pressure.

In most cases one has to deal with the normal boiling points in physico-chemical measurements, and when any boiling point other than this is recorded, the pressure at which it was determined must also be recorded along with it.

The usual method for the determination of the boiling point consists in heating a liquid in a distillation flask with a long neck. The thermometer is placed through a cork in the neck, so that the bulb and the whole of the thread are immersed in the vapour of the boiling liquid. Irregular boiling, *i.e.* "bumping," is prevented by placing a few pieces of platinum foil in the liquid. Since the boiling point depends on the pressure, this must be stated along with the result obtained. The normal boiling point, *i.e.* the boiling point at 760 mm. of mercury pressure, can be obtained from the boiling point at other pressures, if they are not far removed from the normal, by use of the expression

$$t_{760}=t_p+k(760-p),$$

where p is the pressure at which the boiling point was determined, t_p is the actually determined boiling point and k is a constant which differs with the substance in question. When only small quantities of a liquid are available, the method for determination of the boiling point must be considerably modified.

A narrow tube containing 2 or 3 drops of the liquid is bound to a thermometer, as in Fig. 58, a thin capillary tube, closed near the bottom, is placed in the liquid, and the whole placed in a bath of water or some other liquid and slowly heated. As the temperature is raised, a few bubbles of vapour will form in the capillary tube, but at the boiling point they will suddenly increase in number and form a continuous thread of small bubbles. When this occurs the temperature is read. Determinations of this kind may be inaccurate by 0·5°–1°·0.

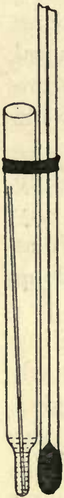


FIG. 58.

Most thermal data are obtained by use of a calorimeter. This piece of apparatus is constructed in many forms adapted to special needs. For the present purpose and for thermochemical determinations, the calorimeter described below is most suitable.

It consists of a double-walled outer vessel A (Fig. 59) made of polished copper, which is fitted with a movable cover C made in two halves. The space between the walls of this vessel is filled with water. Standing inside A, supported on three pointed corks *d*, is a cylindrical vessel B of about 1½ litres capacity, and made of silver or silvered copper. This vessel is prevented from touching the sides of the outer vessel A by means of thin cork wedges *w*, which are cemented on to the walls of the outer vessel. A third vessel O, of about 750 c.c. capacity, and made of silver or platinum, stands inside B, isolated from it by cork supports *s*. This third vessel is the calorimeter proper, *i.e.* the vessel in which the actual measurement takes place; the other vessels are to prevent the access of heat to O from the outside, and the loss of heat from O by radiation during the experiment.

The vessel O is provided with a stirrer made of the same material as the vessel itself. The outside vessel is provided with a stirrer *m*, and is also surrounded with a layer of thick felt.

For most purposes thermometers reading to $\frac{1}{50}^\circ$ are sufficiently sharp reading for the determinations considered in this chapter; occasionally, however, where only small amounts of substances are available, or where the temperature change is very small, Beckmann thermometers must be used. Where this is necessary, note will be made of the fact in the following descriptions.

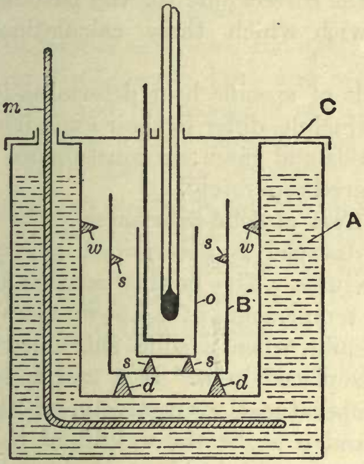


FIG. 59.

3. Determination of Specific Heat

Specific Heat is defined as the quantity of heat, measured in calories, which will raise the temperature of 1 gram of a substance through 1°. Since the quantity of heat required to raise 1 gram of a substance through

1° varies with the temperature, it follows that the specific heat also varies with the temperature. Hence, in stating the specific heat of a substance, it is necessary to specify the temperature at which it has been determined, and, in using the values of specific heat in calculating further quantities, care must always be taken that the value used is the correct one for the particular range of temperature with which these calculations are concerned.

The methods of specific heat determination, although the same in principle, differ in their experimental details for solids, liquids and gases; in consequence of this they will be considered separately.

(*a*) **Specific Heat of Solid Substances.** The specific heat of a solid substance is determined generally by the method of mixtures. This method consists in measuring the change in temperature of a known mass of water, or some other liquid, when a solid substance at a known temperature is placed in it. If t_1 and t_2 be the initial and final temperatures, respectively, of the water or other liquid, and if m be the weight of the liquid and s its specific heat, m_1 the weight of the solid substance which has been heated to a temperature t_3, and s_1 its specific heat, then the solid, on cooling from t_3 to t_2, has given up a quantity of heat represented by $m_1s_1(t_3-t_2)$. This quantity of heat has been used up in raising the temperature of the liquid in the calorimeter, the calorimeter, the stirrer and the thermometer, from t_1 to t_2, and is represented by

$$ms(t_2-t_1)+m_2s_2(t_2-t_1)+m_3s_3(t_2-t_1)+m_4s_4(t_2-t_1),$$

where m_2, m_3, m_4, s_2, s_3 and s_4 are the weights and specific heats of the inner vessel of the calorimeter, stirrer and thermometer respectively. The specific heat of the substance is obtained by equating these two equal quantities of heat.

$$m_1s_1(t_3-t_2)$$
$$=ms(t_2-t_1)+m_2s_2(t_2-t_1)+m_3s_3(t_2-t_1)+m_4s_4(t_2-t_1),$$

from which

$$s_1=\frac{(t_2-t_1)(sm+s_2m_2+s_3m_3+s_4m_4)}{m_1(t_3-t_2)}.$$

Generally the factors s_2m_2, s_3m_3 and s_4m_4, representing the products of the specific heat and weight of the calorimeter, stirrer and thermometer, are substituted in the equation by the water value of the calorimeter. This may be determined experimentally, or calculated from the weights and specific heats, but once determined it serves for all measurements, and is simply added to the weight of water in the calorimeter, and multiplied along with the weight of water by the temperature change. The equation then becomes

$$m_1s_1(t_3-t_2)=(m+w)s(t_2-t_1),$$

where s is the specific heat of water and w the water value of the calorimeter, stirrer and thermometer. Of course, if water is not used in the calorimeter, but some other liquid, then the above equation does not hold. The expression then becomes

$$m_1s_1(t_3-t_2)=m(t_2-t_1)s_l+w(t_2-t_1)s,$$

where s_l is the specific heat of the liquid in the calorimeter, and s that of water. If a large number of determinations have to be made with a liquid other than water in the calorimeter, *e.g.* aniline, it will save much calculation to determine the aniline value of the calorimeter instead of the water value.

To determine the water value of a calorimeter experimentally: fill the outer vessel with water, and place the second vessel in position and allow to stand until the temperature of the water has become that of the air. This may take several hours, and it is therefore expedient to fill the calorimeter the day before it is to be used. Then weigh the inmost vessel, *i.e.* the calorimeter proper, place about 250 c.c. of distilled water into it, and weigh again to the nearest centigram. Place it in the calorimeter and allow it to stand for about 15 minutes, so that its temperature may approach that of the outer walls. Next heat about 250 c.c. of distilled water in a glass flask to about 65°, and place the flask in a silver vessel similar to the innermost calorimeter vessel. Now read the temperature of the water in the calorimeter and that in the flask every minute, stirring all the time, and noting both the time and temperature. Take these readings for about 10 minutes, and then pour the hot water into the cold water in the calorimeter, and stir; note the time at which the addition is made, and then read the temperature again every minute, until the temperature, which at first rose irregularly, falls perfectly regularly. Then weigh the calorimeter and water again, to get the weight of hot water added.

If w_1 be the weight of cold water and t_1 its temperature at the moment of mixing, w_2 the weight of hot water and t_2 its temperature at the moment of mixing, W the water value of the calorimeter, thermometer and stirrer, and t_3 the temperature after mixing, then assuming the specific heat of water to be unity,

$$(w_1+\mathsf{W})(t_3-t_1)=w_2(t_2-t_3);$$

or

$$\mathsf{W}=\frac{w_2(t_2-t_3)-w_1(t_3-t_1)}{(t_3-t_1)}.$$

It will generally be observed that the temperature of liquids is not constant under ordinary circumstances, but is either falling or rising in a perfectly regular manner. If, then, a series of determinations of the temperatures of a liquid at stated intervals be obtained, it is always possible to arrive at the temperature at some period in the near future, by extrapolation. Such is the method which must be adopted to arrive at the temperatures at the actual moment of mixing in the above described experiment. If the temperature readings recorded in the above experiment are plotted as ordinates against the time as abscissae, two curves can be obtained, representing the rates of cooling or heating of the two liquids, and if these curves be produced to the point representing the time of mixing of the two quantities of water, the temperatures at mixing can be obtained from the curve. This is, perhaps, clearer from a diagram; suppose in Fig. 60 the points represent the temperatures at the 1st, 2nd, 3rd, 4th, 5th, 6th and 7th minutes in each case, and that the mixing took place at the 8th minute, then by producing the curves through the points 1–7 to the 8th point, we shall have the true temperatures t_1 and t_2 of the cold and hot water respectively. The mixed liquids are at a higher temperature than the surrounding vessels, and will consequently lose heat by radiation, so that the highest temperature reading will be somewhat less than the correct value. The true temperature may be obtained by plotting the times and temperature readings taken after the mixing. It will be found at first that the temperature quickly rises to a maximum, and then falls regularly. If a curve be drawn through the regular points and produced backward to the 8th minute, *i.e.* the moment of mixing, it will give the correct value for t_3. The values $(t_3 - t_1)$ and $(t_2 - t_3)$ can then be directly read from the curves, as illustrated in Fig. 60. The water value obtained by this method is a mean value, applicable strictly only over the range of temperature for which it has been determined, and if experiments are to be made over temperatures differing widely from these, the value should be re-determined at those temperatures. Generally speaking, however, the water value, once determined over temperatures approximating to those usually employed, will serve for all but the most exact experiments.

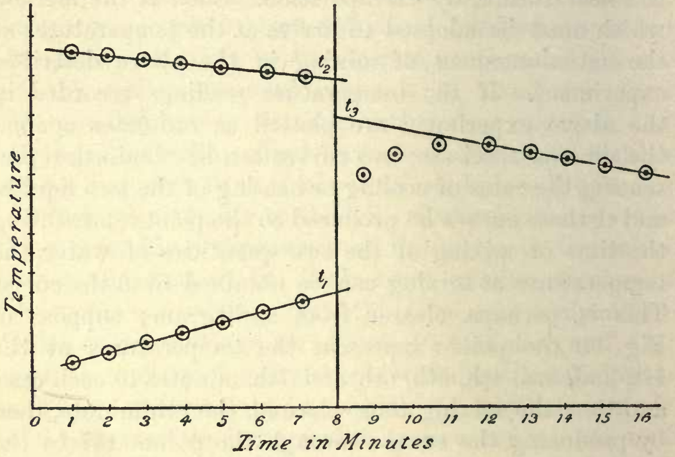


Fig. 60.

Experiment

Determine the Specific Heat of Silver. Fit up the calorimeter as described, and determine its water value if this is not known. Place about 200 c.c. of water in the innermost vessel, and weigh it to the nearest centigram. Then place the cover on the calorimeter and insert a thermometer, reading to $\frac{1}{50}$°, through the hole in the lid, so that its bulb is completely immersed in the water. Then weigh out about 20 grams of silver; this is best used in a granular form. The silver must now be heated to a known temperature, and transferred to the water in the calorimeter without loss of heat. This is best done by a device due to Crompton. The method consists in placing the silver in the inner tube A (Fig. 61) of a double-walled glass vessel. A small quantity of a liquid of fairly high boiling point is placed in the outer vessel, together with some bits of platinum foil to prevent "bumping," and briskly boiled. In this experiment aniline is a suitable liquid to use. After some fifteen or twenty minutes, the silver will have been raised to the boiling point of the liquid, *i.e.* the temperature of the vapour which has surrounded it; the condenser is then removed from C, and the silver is tipped directly from A into the calorimeter, care being taken to avoid splashing. The construction of the tube prevents the heating liquid flowing out. As soon as the silver has been added, stir slowly, and make series of temperature readings similar to those made with the water at the beginning of the experiment, and in the manner described above. Then, if W is the water value of the calorimeter, w the weight of silver, w_1 that of the water, t the initial temperature of the silver, t_1 that of the water, and t_2 the final temperature, s the specific heat of the silver, and s_1 the mean specific heat of water over the range of temperature $t_1 - t_2$,

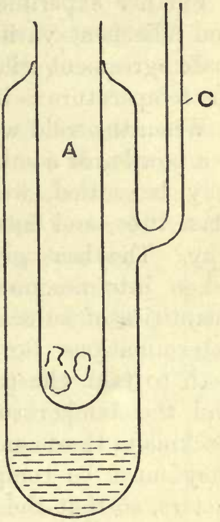


FIG. 61.

$$(t_2 - t_1) \cdot s_1 \cdot (\mathrm{W} + w_1) = sw(t - t_2),$$

$$s = \frac{(\mathrm{W} + w_1)(t_2 - t_1)s_1}{w(t - t_2)}.$$

A table of specific heats of water at various temperatures is given in the Appendix (Table VIII.).

Having obtained the specific heat, use it to test the truth of Dulong and Petit's law:

$$\text{Atomic weight} \times \text{specific heat} = 6{\cdot}4.$$

Further experiments may be made with aluminium and silicon at various temperatures, and their approximate agreement with Dulong and Petit's law observed as the temperature is increased.

When the solid whose specific heat is to be determined is a powder or a substance which is attacked by water, it may be sealed, weighed and heated in a thin-walled glass tube, and introduced into the calorimeter in this way. The heat given up by the glass tube must be taken into account in the calculation If only small quantities of substances are available for specific heat determinations, Beckmann thermometers must be used, both to take the temperature of the heated substance and the temperature change of the calorimeter. If Beckmann thermometers are used in this class of work they must be compared with short, standard thermometers, so that the exact value of their scales becomes known.

In the case of a substance which is either attacked by, or dissolved in, water, some other liquid may be used in the calorimeter, *e.g.* aniline, toluene or turpentine. Of these liquids aniline is to be preferred. Its specific heat does not vary much with temperature, and has been throughly investigated by Griffiths (*Phil. Mag.* 39, 47 and 143). Indeed, aniline is to be preferred to water for all determinations where it does not react with the substance under investigation, because its boiling point is much higher than that of water, and its specific heat is only about one-half that of water. The former fact allows of determinations being made at higher temperatures than are possible with water, and the low specific heat occasions much larger changes of temperature, which obviously lead to more accurate results. The specific heat of aniline for temperatures between 15°–52° is given by the expression

$$s = 0{\cdot}5156 + (t - 20) \times 0{\cdot}0004 + (t - 20)^2 \times 0{\cdot}000002.$$

Table IX. Appendix, gives the specific heat of aniline at various temperatures.

Aniline, which is to be used for thermal determinations, should be purified by the method due to Hantzsch and Fresse (*Ber.* 27, 2529). This consists in boiling it with 10 per cent. of its weight of acetone for ten hours, and then carefully fractionating. Aniline purified in this way is free from sulphur compounds and does not readily colour in the air.

(*b*) **Specific Heat of Liquids.** The specific heat of liquids may be determined either by the method of mixtures or by the method of cooling.

The method of mixtures is applied to liquids in exactly the same way that it is applied to solids. The liquid is heated in a thin-walled glass tube, fitted with a cork which carries a thermometer and a stirrer, as illustrated in Fig. 62. The tube containing the liquid is placed in a bath at a suitably high temperature, and kept there until it has taken on the temperature, then it is supported inside a silver vessel, similar to the calorimeter vessel, and its temperature is taken every minute for ten minutes. It is then plunged into the water of the calorimeter, whose temperature has been taken in the same way; both

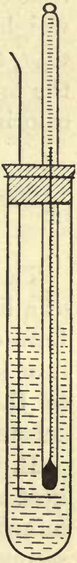


Fig. 62.

liquids are kept stirred, and the temperature of the water in the calorimeter is taken until it is falling regularly. The method of calculation is exactly the same as in the preceding case.

In the case of liquids which are easily obtained in large quantities, the method of mixtures may be applied in the following way. The water in the calorimeter is substituted by the liquid in question, and a known weight of a metal of known specific heat and at a known temperature is added to it, and the temperature change noted, exactly as in the determination of the specific heat of a solid. If, now, w, t and s are respectively the weight, temperature and specific heat of the metal, and w_1, t_1 and s_1 the corresponding quantities for the liquid, t_2 the final temperature and W the water equivalent of the calorimeter, then

$$\mathsf{W}(t_2-t_1)+w_1s_1(t_2-t_1)=ws(t-t_2)$$

or

$$s_1=\frac{ws(t-t_2)-\mathsf{W}(t_2-t_1)}{w_1(t_2-t_1)}.$$

The principle of the determination of the specific heat of a liquid by the method of cooling, is based on Newton's Law of Cooling, which states, "That the quantity of heat lost, by a substance in a given time, is proportional to the mean difference of temperature between the substance and its surroundings."

If, then, the time T, required by a liquid A of specific heat s to fall from a temperature t_2 to one t_1, be determined, and compared with the time T_1, required by a second liquid B of specific heat s_1 to cool through the same temperature interval, under the same condition, the relationship:

Heat lost by liquid A : heat lost by liquid B

$$:: ws(t_2-t_1) : w_1s_1(t_2-t_1)$$

will be obtained, where w and w_1 are the weights of A and B respectively. Also

Heat lost by liquid A : heat lost by liquid B :: T : T_1,

hence $$\frac{ws(t_2-t_1)}{w_1s_1(t_2-t_1)}=\frac{T}{T_1}; \quad \therefore \frac{ws}{w_1s_1}=\frac{T}{T_1}.$$

If, now, the specific heat of the liquid A be known, say (for) water, $s=1$, then

$$s_1=\frac{w}{w_1}\cdot\frac{T_1}{T}.$$

To determine the specific heat of a liquid by this method, about 20 grams of water are weighed out to the nearest centigram, in a tube fitted with thermometer and stirrer (see Fig. 62). It is then heated to a temperature slightly above 40° and placed in an empty calorimeter, which is surrounded with ice, and the time required for its temperature to fall from 40° to 30° is taken, the liquid being stirred slowly all the while. The experiment is then repeated with about the same volume of the liquid whose specific heat is to be determined, the conditions being kept identical with those of the first part of the experiment. The specific heat is then calculated by the formula given above.

EXPERIMENTS

(i) *Determine the Specific Heat of Ethyl Alcohol.* Use the method of mixtures for this experiment, making use of about 15 c.c. of absolute alcohol, which must be heated to about 40° in a thin-walled tube. Place about 200 c.c. of water in the calorimeter, and determine the temperature change by means of a Beckmann thermometer. The specific heat of the glass tube must be determined before the calculation can be carried out.

(ii) *Determine the Specific Heat of Nitrobenzene.* Use the method of mixtures for this experiment. Place about 150 c.c. of nitrobenzene in the calorimeter, and heat up about fifty grams of granulated copper to about 184° by using an aniline bath, as described under the specific heat of solids. Add the copper to the nitrobenzene and determine the temperature change. Calculate the specific heat by the usual formula, being given that the mean specific heat of copper is 0·0966 between 20°–200°.

(iii) *Determine the Specific Heat of Acetone.* Use the method of cooling for this experiment. Weigh out 10–15 grams of acetone, heat it to 36°–37° in a tube, as described above, place in a calorimeter surrounded by ice, taking care that the tube does not touch the walls of the calorimeter and occupies a central position in the calorimeter. Allow it to cool to 35° and then determine the time required for it to cool to 25°, stirring slowly all the while. Make a similar determination for the same volume of water. Assuming the specific heat of water is unity, calculate the specific heat of acetone by the method indicated.

(*c*) **Specific Heat of Gases.** The specific heat of gases requires more apparatus than is usually available in most chemical laboratories for its determination, furthermore, it is not an experiment at all easy of performance; it will therefore not be considered here. For physico-chemical purposes, the ratio of the specific heat of gases at constant volume and constant pressure is of more importance. For methods of determining this ratio see Chapter VI.

4. Determination of Latent Heat of Fusion

The latent heat of fusion is the quantity of heat required to convert one gram of a solid substance, at its melting point, into the liquid state at the same temperature.

The latent heat of fusion is determined generally by the method of mixtures. A weighed quantity of the substance is raised to a known temperature above its melting point, and added to a known quantity of water or other liquid at a known temperature in a calorimeter, and the temperature change noted. It will be obvious that, before the latent heat can be determined, it is necessary to know the specific heats of the substance both in the liquid and solid forms, and also the melting point must be accurately known. Suppose the melting point of the substance be t°, and that it is melted and raised to a temperature t_1° before it is added to the liquid in the calorimeter. Let t_2° be the final temperature of the liquid in the calorimeter. Then the heat given out by the substance added to the liquid in the calorimeter is made up of three distinct quantities: (1) the heat given up whilst the molten solid falls in temperature from t_1° to the melting point, which is equal to $ws(t_1-t)$, where w is the weight of the solid and s the specific heat of the substance in the molten condition; (2) the heat given up at the melting point, as the liquid becomes solid, *i.e.* wL, where L is the latent heat of fusion; and (3) the heat given out as the solid substance cools from the melting point to the final temperature of the experiment. This is equal to $ws_1(t-t_2)$, where s_1 is the specific heat of the substance in the solid condition. The sum of these three quantities of heat is equal to the heat gained by the liquid in the calorimeter and the calorimeter itself, in raising them from their initial temperature t_3 to the final temperature t_2. If W be the weight of liquid in the calorimeter, and s_3 its specific heat, and N be the water equivalent of the calorimeter, then

$$(\mathsf{W}s_3+\mathsf{N})(t_2-t_3)=w\mathsf{L}+ws_1(t-t_2)+ws(t_1-t)$$

or

$$\mathsf{L}=\frac{ws_1(t-t_2)+ws(t_1-t)-(\mathsf{W}s_3+\mathsf{N})(t_2-t_3)}{w}.$$

EXPERIMENT

Determine the Latent Heat of Fusion of p-Toluidine. Before proceeding to the actual determination of the latent heat, the melting point, and specific heat of liquid and of solid *p*-toluidine must be determined.

Determine the melting point by the method given in section 1 of this chapter, and *not* in a capillary tube.

Having obtained the melting point, place about 10 grams of *p*-toluidine in a previously weighed thin-walled tube, melt it down to a compact mass, and when it has cooled, weigh again. Then draw off the top of the tube so that the substance is sealed up in the bulb, and weigh again. From the three weighings, the weight of the *p*-toluidine and the bulb can be obtained.

Place the bulb in a heating tube (Fig. 61) and raise it to a temperature about 35°, *i.e.* somewhat below the melting point of *p*-toluidine; use boiling ether in the heating jacket to obtain this temperature. When the bulb and contents have attained this temperature, *i.e.* in about 20 minutes, tip them into the calorimeter, which contains about 300 c.c. of aniline whose weight and temperature are known. Stir well, and determine the final temperature by the method indicated. The temperature determinations throughout this experiment should be made with Beckmann thermometers. From the data thus obtained, calculate the mean specific heat of solid *p*-toluidine.

Remove and clean the bulb containing the *p*-toluidine and re-heat it, this time using boiling alcohol as the heating bath; keep it in this bath until its temperature is constant. Meanwhile, heat the aniline in the calorimeter to 50°, *i.e.* above the melting point of *p*-toluidine. When the temperatures of the aniline and the *p*-toluidine are defined, add the bulb to the aniline and stir until the final temperature is defined. From the data thus obtained, since the *p*-toluidine has not solidified, calculate the specific heat of molten *p*-toluidine.

All the necessary contributory data having been determined, the actual determination of the latent heat can next be proceeded with. Cool the aniline in the calorimeter to atmospheric temperature, and heat the toluidine up to the boiling point of alcohol again. When the temperatures of both are defined, add the toluidine to the aniline and stir until the final temperature is obtained. The latent heat can now be calculated, since this time the toluidine has solidified. The water equivalent of the calorimeter, and the heat due to the glass tube must be taken into account in all calculations; (the specific heat of glass may be taken as 0·20). The order of the various determinations as described above is the natural one, but it will save time if they are made in the following order: (1) determination of the melting point; (2) determination of the specific heat of the solid; (3) total heat change from 80° to the low temperature; (4) specific heat of molten toluidine. In this way the loss of time in waiting for the hot aniline to cool will be avoided. The same Beckmann thermometer may be used for determinations 2 and 3, but another one must be used for determination 4, or the original one must be re-set.

Calculate the latent heat of fusion of *p*-toluidine from the Molecular Lowering Constant (see Chapter VII.), by means of the expression

$$L = \frac{0{\cdot}02T^2}{K},$$

and compare it with your result. The value of K for *p*-toluidine is 53, and T is the freezing point in absolute degrees.

The following substances are suitable for alternative or additional experiments: Naphthalene, M.P. 79°; Azobenzene, M.P. 68°; *p*-dichlorobenzene, M.P. 53°; and *p*-nitrotoluene, M.P. 54°.

5. Determination of the Latent Heat of Vaporisation

The Latent Heat of Vaporisation is the quantity of heat required to convert one gram of a liquid at its boiling point into vapour at the same temperature.

There are two methods which can be considered here for this determination: (i) Calorimetric Method, (ii) Campbell Brown's Method.

(i) **Calorimetric Method.** This method is open to serious inaccuracies which are often difficult to remove, particularly in the case of liquids of high boiling point. The method consists in condensing a known weight of vapour at its boiling point in a calorimeter, and observing the temperature change of the calorimeter liquid.

For the determination, the ordinary calorimeter will serve, but the inside vessel must be fitted with a silver spiral A (Fig. 63), which terminates at the bottom in a bulb B, for holding the condensed vapour. The bulb is open to the air by a tube **E**. The liquid whose latent heat is to be determined is contained in a flask **C**, which has an outlet tube passing through the bottom, as indicated in the diagram. The flask is placed above the calorimeter, thus ensuring that the vapour does not condense until it reaches the calorimeter, and is heated by a ring burner **D**. The calorimeter is protected from the heat of the burner by placing a thick piece of wood **W**, covered with asbestos on its lower side, and with copper gauze on its upper side, above the ordinary calorimeter cover. The weight of the vapour condensed, is obtained by weighing the silver condenser before and after the experiment.

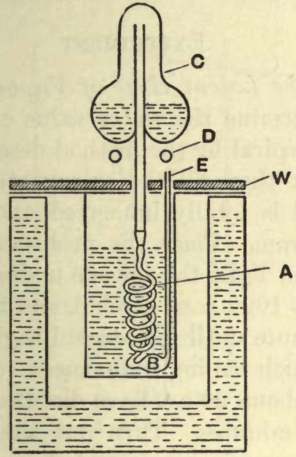


FIG. 63.

If **L** be the latent heat of vaporisation, s the specific heat of the condensed liquid and w its weight, t the boiling point, w_1 the weight of liquid in the calorimeter, s_1 its specific heat, t_1 its initial temperature and t_2 its final temperature, and W the water value of the calorimeter and spiral, then

$$W(t_2-t_1)+w_1s_1(t_2-t_1)=Lw+ws(t-t_2),$$

$$L=\frac{(W+w_1s_1)(t_2-t_1)-ws(t-t_2)}{w}.$$

EXPERIMENT

Determine the Latent Heat of Vaporisation of Ethyl Alcohol. Determine the water value of the calorimeter and the silver spiral by the method described in section 3 (this chapter); then fill the calorimeter with water so that the spiral is totally immersed, and weigh it to the nearest centigram. Place the protecting covers on the calorimeter, and light the burner under the flask, which contains about 100 c.c. of alcohol, and take the temperature every minute until the alcohol begins to boil, noting the time at which boiling commences. Allow the alcohol to boil until about 20 c.c. have distilled over, this ought to take 8–10 minutes. Turn out the flame and take the temperature again over a period of about 10 minutes; note the time at which the flame is turned out. Since the addition of the heated substance cannot be said to take place at a given moment, but extends over a considerable period, the time at which half the vapour has been added must be taken as the time of the addition of the hot substance, for purposes of calculation.

The method of arriving at the initial temperature is the same as previously indicated, that of reaching the final temperature is indicated in Fig. 64. The initial temperature is given by b, the final temperature by a, and the difference (t_2-t_1) by the distance ab.

When the temperature measurements have been completed, remove the spiral, carefully dry it and weigh it.

This will give the weight of the condensed vapour. The calculation must then be carried out as indicated above.

(ii) **Campbell Brown's Method.** The method just described is extremely laborious, and, except in the hands of an expert experimenter, does not yield trustworthy results. A method much easier from the experimental point of view was devised by Ramsay and Marshall, which, however, was only comparative, and the accuracy of its results depended on the purity of benzene, which was used as the standard of comparison. This method has been modified by Campbell Brown (*J.C.S.* 987, 1903) into an absolute method. It consists in heating a liquid at its boiling point by an electrically heated wire, and weighing the amount of liquid boiled off by a known amount of electrical energy.

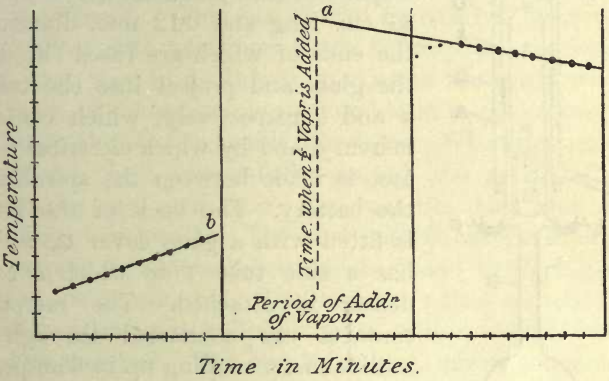


FIG. 64.

The apparatus consists of a round-bottomed flask C (Fig. 65) of about 100 c.c. capacity, fitted with a neck B which is expanded at the top A to about 3·5 cm. diameter. The neck is also fitted with two side tubes *a* and *b*, which are bent as indicated in the diagram. The expanded neck is fitted with a ground glass stopper S, which has a small hole at the top *h*. The experimental tube D is a thin glass cylindrical vessel, pierced by a small hole *f* at the top, and is about 10 cm. long and 2·5 cm. diameter. It contains a spiral of thin platinum wire P about 31 cm. long and 0·12 mm. diameter, the ends of which are fused through the glass and project into the tubes *a* and *b* respectively, which contain mercury, and by which electrical contact is made between the spiral and the battery. The neck of the flask is fitted with a glass cover G, which has a side tube T to which a condenser is attached. The mercury contacts are connected through a milliammeter reading up to 6 amperes and an adjustable resistance with a battery of four accumulator cells. A voltmeter, reading to $\frac{1}{100}$ volt is also connected to these contacts in a separate circuit provided with a key.

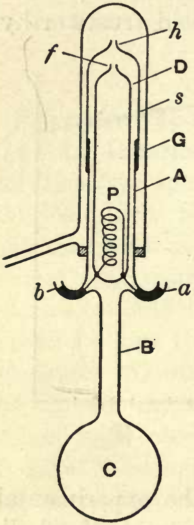


FIG. 65.

To carry out a determination with this apparatus, about 50 c.c. of the liquid are placed in the flask C, then the experimental tube D is carefully weighed, and about three-fourths filled with the liquid, and again weighed. It is then placed in position, and the cap and cover glass G are replaced, and the liquid in C is caused to boil briskly. This is allowed to go on for exactly 20 minutes, then the boiling is stopped, and when D is cool enough, it is removed and re-weighed. It will be found to have lost slightly in weight. This loss must be used to correct the final loss in the experiment. The tube and caps are replaced, and the liquid in C set boiling; in about 15 minutes the liquid in D will have been raised to the boiling point. The current is then switched on, and the liquid in D will immediately begin to boil. The success of the experiment depends on the boiling in D occurring simultaneously with the switching on of the current. This can always be ensured by coating the spiral with platinum black before the experiment. The best way to do this is to moisten the spiral with a solution of chloroplatinic acid, and then to pass a current through the wire to heat it to redness. When the experiment has been successfully started, the ammeter and voltmeter are read every two minutes, the time and readings being noted. The most suitable current strength to employ is 3–5 amperes, which should be kept going for about 20 minutes. The current is then switched off and C is stopped boiling. Then D is removed, cooled and re-weighed. The loss in weight, minus a quantity proportional to the loss at the previous heating, represents the quantity of liquid evaporated by the electrical energy expended, since the liquid in D is kept at its boiling point by the vapour from C, and the electrical energy is only used to perform the actual vaporisation at the boiling point. The correction factor, which must be applied to the loss of weight of the tube D, is obtained thus: suppose in the previous heating, the liquid in D loses w grams in t minutes, and the actual determination takes t_1 minutes, then the amount to be subtracted from the total loss of weight is equal to $\frac{wt_1}{t}$.

If E is the mean electromotive force between the ends of the spiral, as given by the voltmeter readings, and C the current strength from the ammeter readings, then

$$R = \frac{E}{C},$$

where R is the resistance of the platinum spiral in ohms.

It is known by Joule's Law that the heating effect of a current is proportional to the product of the resistance in ohms, the time in seconds, and the square of the current strength in amperes; *i.e.*

$$H = C^2Rt \times 0{\cdot}24.$$

Hence, by this expression, we get the quantity of heat used up in vaporising W grams of the liquid, where W is the corrected loss of weight of the tube. If, then, L represent the latent heat of vaporisation,

$$L = \frac{H}{W}.$$

EXPERIMENT

Determine the Latent Heat of Vaporisation of Ether. Prepare pure anhydrous ether for this experiment by shaking up ordinary ether with two separate quantities each of half its own volume of water; separate, and allow to stand over calcium chloride for 3–4 hours, then place over sodium wire for 2–3 hours, and finally distil from a flask containing sodium wire.

Use three accumulators as the source of current, with a resistance of 1–3 ohms in the circuit, so that the ammeter registers 0·5–1 ampere. Allow the current to flow for 15 minutes. It is expedient to carry the preliminary heating over the same length of time.

Calculate the latent heat of vaporisation by the formulae given above, and compare it with the value obtained from the molecular rise of boiling point.

$$L = \frac{0{\cdot}02T^2}{K};$$

K for ether is 21·5, and T is the boiling point in absolute degrees. From your results calculate the molecular latent heat of vaporisation ML, where M is the molecular weight, and determine the value of the expression $\frac{ML}{T}$, which, according to Trouton's Rule, should be about 21, and should have the same value for all liquids.

Further experiments may be carried out with benzene, alcohol and methyl-acetate.

APPENDIX

TABLE I

RELATION BETWEEN VOLUME AND APPARENT WEIGHT

Water			Mercury	
Temperature	Apparent Weight of 1 c.c. of Water	Volume of an Apparent Gram	Apparent Weight of 1 c.c. of Mercury	Volume of an Apparent Gram
10°	0·9986	1·00133	13·5782	0·073683
11°	0·9985	1·00143	13·5757	0·073697
12°	0·9984	1·00154	13·5733	0·073710
13°	0·9983	1·00166	13·5708	0·073724
14°	0·9982	1·00180	13·5683	0·073737
15°	0·9981	1·00193	13·5659	0·073750
16°	0·9979	1·00209	13·5634	0·073764
17°	0·9977	1·00226	13·5509	0·073777
18°	0·9976	1·00244	13·5489	0·073790
19°	0·9974	1·00263	13·5460	0·073804
20°	0·9972	1·00283	13·5435	0·073817
21°	0·9970	1·00305	13·5411	0·073831
22°	0·9968	1·00327	13·5386	0·073844
23°	0·9965	1·00350	13·5361	0·073857
24°	0·9963	1·00375	13·5336	0·073871
25°	0·9960	1·00400	13·5312	0·073884

TABLE II

DENSITY OF WATER

Temperature	Density	Temperature	Density
0°	0·99986	21°	0·99802
1°	0·99992	22°	0·99779
2°	0·99997	23°	0·99756
3°	0·99999	24°	0·99732
4°	1·00000	25°	0·99707
5°	0·99999	26°	0·99681
6°	0·99996	27°	0·99653
7°	0·99993	28°	0·99626
8°	0·99987	29°	0·99597
9°	0·99981	30°	0·99567
10°	0·99973	31°	0·99537
11°	0·99963	32°	0·99505
12°	0·99952	33°	0·99473
13°	0·99940	34°	0·99440
14°	0·99927	35°	0·99406
15°	0·99913	40°	0·99224
16°	0·99898	50°	0·98807
17°	0·99880	60°	0·98324
18°	0·99862	70°	0·97781
19°	0·99843	80°	0·97183
20°	0·99823	90°	0·96534

TABLE III

BOILING POINT OF WATER AT VARIOUS PRESSURES

Pressure	Temperature	Pressure	Temperature	Pressure	Temperature
725 mm.	98°·68	745 mm.	99°·44	765 mm.	100°·18
726 „	98°·72	746 „	99°·48	766 „	100°·22
727 „	98°·76	747 „	99°·52	767 „	100°·26
728 „	98°·80	748 „	99°·55	768 „	100°·29
729 „	98°·84	749 „	99°·59	769 „	100°·33
730 „	98°·87	750 „	99°·63	770 „	100°·37
731 „	98°·92	751 „	99°·67	771 „	100°·40
732 „	98°·95	752 „	99°·70	772 „	100°·44
733 „	98°·99	753 „	99°·74	773 „	100°·47
734 „	99°·03	754 „	99°·78	774 „	100°·51
735 „	99°·07	755 „	99°·82	775 „	100°·55
736 „	99°·10	756 „	99°·85	776 „	100°·58
737 „	99°·14	757 „	99°·89	777 „	100°·62
738 „	99°·18	758 „	99°·93	778 „	100°·66
739 „	99°·22	759 „	99°·96	779 „	100°·69
740 „	99°·26	760 „	100°·00	780 „	100°·73
741 „	99°·29	761 „	100°·04	781 „	100°·76
742 „	99°·33	762 „	100°·07	782 „	100°·80
743 „	99°·36	763 „	100°·11	783 „	100°·84
744 „	99°·41	764 „	100°·15	784 „	100°·87

TABLE IV

VAPOUR TENSION OF MERCURY

Temperature	Vapour Tension	Temperature	Vapour Tension
70°	0·24 mm.	170°	8·09 mm.
80°	0·35 „	180°	11·00 „
90°	0·51 „	190°	14·84 „
100°	0·74 „	200°	19·90 „
110°	1·07 „	210°	26·35 „
120°	1·53 „	220°	34·70 „
130°	2·17 „	230°	45·35 „
140°	3·06 „	240°	58·82 „
150°	4·27 „	250°	75·75 „
160°	5·90 „	260°	96·73 „

TABLE V

TENSION OF AQUEOUS VAPOUR

Temperature	Vapour Tension	Temperature	Vapour Tension
4°	6·0 mm.	19°	16·4 mm.
5°	6·5 „	20°	17·4 „
6°	6·9 „	21°	18·5 „
7°	7·5 „	22°	19·6 „
8°	8·0 „	23°	20·9 „
9°	8·5 „	24°	22·2 „
10°	9·2 „	25°	23·5 „
11°	9·8 „	26°	25·0 „
12°	10·5 „	27°	26·5 „
13°	11·2 „	28°	28·1 „
14°	11·9 „	29°	29·8 „
15°	12·7 „	30°	31·5 „
16°	13·5 „	31°	33·4 „
17°	14·4 „	32°	35·4 „
18°	15·3 „	33°	37·4 „

TABLE VI

SURFACE TENSION OF WATER

Temperature	Specific Cohesion	Surface Tension in mg. per mm.	Surface Tension in dynes per cm.
10°	15·103	7·541	74·00
11°	15·074	7·526	73·86
12°	15·045	7·510	73·70
13°	15·015	7·495	73·56
14°	14·985	7·480	73·41
15°	14·961	7·465	73·22
16°	14·931	7·450	73·11
17°	14·900	7·434	72·96
18°	14·877	7·420	72·82
19°	14·846	7·404	72·66
20°	14·823	7·439	72·53
21°	14·796	7·374	72·37
22°	14·769	7·359	72·22
23°	14·739	7·344	72·08
24°	14·710	7·329	71·93
25°	14·688	7·314	71·78
26°	14·656	7·298	71·63
27°	14·632	7·283	71·48
28°	14·604	7·268	71·33
29°	14·579	7·253	71·18
30°	14·566	7·238	71·03
31°	14·528	7·222	70·88
32°	14·504	7·208	70·74

TABLE VII

WAVE LENGTHS OF SPECTRUM LINES OF METALS

The strongest lines are printed in heavy type

Metal	Colour of Line	Wave Length in Ängstrom Units
Barium	violet	3910·0
	violet	3993·6
	violet	4130·9
	blue	4554·4
	green	4934·2
	green	**5535·7**
	green	5777·8
	yellow	5853·9
	orange	6141·9
	red	6497·0
Caesium	blue	**4554·4**
	blue	**4593·3**
	green	5664·0
	yellow	5845·1
	orange	6010·6
	orange	6210·4
	red	6723·6
	red	6973·9
Calcium	blue	4226·9
	green	**5588·9**
	orange-red	6162·5
	red	6499·8
Indium	violet-blue	**4101·8**
	indigo-blue	**4511·1**

Metal	Colour of Line	Wave Length in Ängstrom Units
Potassium	violet	4044·3
	yellow	5782·7
	red	6938·8
	red	**7668·5**
	red	**7701·9**
Copper	violet	4022·8
	blue	4275·3
	green	5105·7
	green	5700·4
	green	5782·3
Lithium	blue	4602·3
	yellow	6103·7
	red	**6708·2**
Sodium	yellow	**5890·2**
	yellow	**5896·1**
Rubidium	violet	4202·0
	violet	4215·7
	green	5724·4
	red	**6298·7**
	red	7805·6
	red	7950·4
Strontium	blue	**4607·5**
	green	**5481·1**
	red	**6408·6**
	red	6550·5
Thallium	green	**5350·6**

TABLE VIII

SPECIFIC HEAT OF WATER

Temperature	Specific Heat	Temperature	Specific Heat
0°	1·0051	55°	1·0051
5°	1·0027	60°	1·0065
10°	1·0010	65°	1·0079
15°	1·0000	70°	1·0092
20°	0·9994	75°	1·0104
25°	0·9993	80°	1·0113
30°	0·9996	85°	1·0119
35°	1·0003	90°	1·0121
40°	1·0013	95°	1·0120
45°	1·0024	98°	1·0120
50°	1·0037	100°	1·0118

TABLE IX

SPECIFIC HEAT OF ANILINE

Temperature	Specific Heat
15°	0·5137
20°	0·5155
25°	0·5175
30°	0·5198
35°	0·5221
40°	0·5244
45°	0·5268
50°	0·5294
52°	0·5304

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